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Chemistry Section

IN ENGLISH TRANSLATION

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THE THERMAL CONDENSATION OF DICHLOROSILANE WITH CHLOROBENZENE

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It has been noted in the literature that phenyldichlorosilane is formed with about 30% yield [1] in the thermal condensation of dichlorosilane with chlorobenzene. In a study of this reaction we were able to establish that the reaction of dichlorosilane with chlorobenzene proceeds in a complex manner. Along with the formation of phenyldichlorosilane by the reaction

$$H_2SiCl_2 + C_6H_5Cl \rightarrow C_6H_5SiHCl_2 + HCl \quad (1)$$

the substitution of the second hydrogen atom attached to the silicon on a phenyl group also takes place; along with this at the high temperatures at which the thermal condensation is carried out a new reaction – substitution of a hydrogen atom attached to the silicon on to a chlorine atom – was to be expected. As a result of this complex manner in which the process occurs diphenyldichlorosilane, phenyltrichlorosilane, benzene and trichlorosilane are present in the reaction products simultaneously with phenyldichlorosilane.

As our investigations have indicated, the yield of reaction products is primarily dependent on temperature. It can be seen from Fig. 1 that the yield of phenyldichlorosilane increased up to a temperature of the order of 640-660° (optimum temperature for reaction 1) reaching 41.7%; at the same time the yield of phenyltrichlorosilane increased to 18.3%. On further increase of temperature up to 700° the yield of phenyldichlorosilane dropped to 12% while the yield of phenyltrichlorosilane continued to rise and reached 26%. Simultaneously, on increasing the temperature, the yield of diphenyldichlorosilane increased initially (to 12.4% at 660°) but fell to 2.5% at 700°.

These facts are evidence that the reaction of dichlorosilane with chlorobenzene proceeds at an increasing rate, therefore silane and chlorosilane were practically absent in the reaction products, while the evolution of hydrogen through the decomposition of dichlorosilane was not detected.

$$C_6H_5SiHCl_2 + C_6H_5Cl \rightarrow (C_6H_5)_2SiCl_2 + HCl, \quad (2)$$

and also side reactions involving the chlorination of chlorosilanes:

$$H_2SiCl_2 + C_6H_5Cl \rightarrow HSiCl_3 + C_6H_6 \quad (3)$$

and

$$C_6H_5SiHCl_2 + C_6H_5Cl \rightarrow C_6H_5SiCl_3 + C_6H_6. \quad (4)$$

It is extremely likely that part of the phenyltrichlorosilane was formed in accordance with the scheme

$$HSiCl_3 + C_6H_5Cl \rightarrow C_6H_5SiCl_3 + HCl. \quad (5)$$

The rates of reactions (3), (4), and (5) increased considerably faster than the rate of reaction (2), and at 680° the rates of formation of phenyltrichlorosilane became nearly equal.

It is hardly possible to explain the formation of trichlorosilane and phenyltrichlorosilane by another route, e.g., by disproportionation reactions

$$2H_2SiCl_2 \rightarrow HSiCl_3 + H_3SiCl \quad (6)$$

or the decomposition of dichlorosilane

$$3H_2SiCl_2 \rightarrow Si + 2HSiCl_3 + 2H_2, \qquad (7)$$

In exactly the same way it is difficult to explain the formation of benzene by reaction schemes other than (3) and (4), e.g., through the pyrolysis of chlorobenzene in a reducing medium. We carried out chlorobenzene pyrolysis experiments in which the yield of benzene did not exceed 9% (pyrolysis in an atmosphere of hydrogen) and 2.2% (pyrolysis in an atmosphere of silane) against 55-60% in the experiments concerned with the formation of phenyldichlorosilane. The low yield of high-boiling products – still residues (2-4%) also testifies to the insignificant role of pyrolytic processes in the production of phenyldichlorosilane.

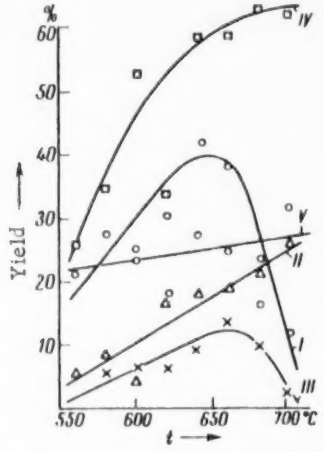

Fig. 1. Temperature dependence of yield of thermal condensation products. I) $C_6H_5SiHCl_2$; II) $C_6H_5SiCl_3$; III) $(C_6H_5)_2 \cdot SiCl_2$: IV) C_6H_6; V) $HSiCl_3$.

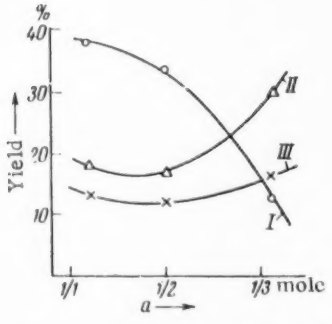

Fig. 3. Dependence of the yield of thermal condensation products on the molar ratio of dichlorosilane to chlorobenzene (a). I) $C_6H_5SiHCl_2$; II) $C_6H_5SiCl_3$; III) $(C_6H_5)_2SiCl_2$.

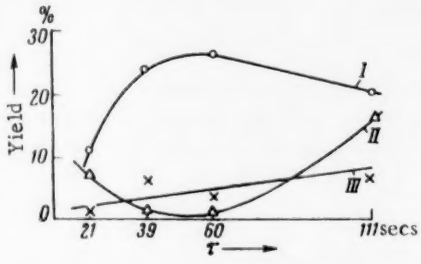

Fig. 2. Dependence of the yield of thermal condensation products on contact time. I) $C_6H_5SiHCl_2$; II) $C_6H_5SiCl_3$; III) $(C_6H_5)_2SiCl_2$.

Experimental data are presented on the dependence of the yields of phenyldichlorosilane, phenyltrichlorosilane, diphenyldichlorosilane, on contact time in Fig. 2, and on the molar ratio of the components in Fig. 3. Under the optimum conditions the over-all yield of these compounds is 74.6%.

EXPERIMENTAL*

1. Condensation of dichlorosilane with chlorobenzene. The mixture of the calculated quantities of dichlorosilane and chlorobenzene was fed from a dropping funnel cooled with dry ice into a quartz tube 24 mm in diameter and 75 mm long provided with an electric heater. The reaction products were condensed in a water condenser, an ice-cooled trap and a trap cooled with a dry ice – acetone mixture in series. Before the commencement of a run the tube was purged with a stream of dry nitrogen. Separation of the liquid reaction products was carried out by three stage rectification. First unreacted dichlorosilane (b. p. 8-10°) and trichlorosilane (b. p. 30-32°) were removed in a low temperature packed column with the equivalent of 37 theoretical plates. Next the residue was rectified in a packed glass column with the equivalent of 26 theoretical plates at atmospheric pressure to remove benzene (b. p. 78-80°), chlorobenzene (b. p. 130-132°), phenyldichlorosilane (b. p. 180-185°) and phenyltrichlorosilane (b. p. 192-199°). The still residue was distilled at a pressure of

*S. A. Platonova and T. A. Klochkova took part in the experimental part of the work.

10 mm to separate the rest of the phenyltrichlorosilane and also the diphenyldichlorosilane (b. p. 146-150°). The composition of the intermediate fractions was calculated from their chlorine content. The results of the experiments carried out are presented in Table 1.

TABLE 1. Thermal Condensation of Chlorobenzene with Dichlorosilane

Run No.	Quantity of dichlorosilane, g	Quantity of chlorobenzene, g	Synthesis temperature, °C	Duration of run, min	Contact time, sec	Molar ratio $\frac{H_2SiCl_2}{C_6H_5Cl}$	Yield of liquid products, g	Yield of reaction products based on dichlorosilane reacted, %					Yield of still residues, wt. %
								trichlorosilane	benzene	phenyldichlorosilane	phenyltrichlorosilane	diphenyldichlorosilane	
1	41	50	560-570	140	40	1:1.1	87	21.1	26.4	20.2	6.4	1.4	2.5
2	41	50	580-590	140	39	1:1.1	81	2.0	35.0	27.8	8.3	5.5	2.5
3	30	37	600-610	96	36		56	23.0	53.0	24.2	4.7	6.5	2.0
4	36	43	600-630	120	38	1:1.1	66	17.2	34.0	30.3	1.3	5.8	4.2
5	88	197	640-650	420	37	1:8.0	275	27.4	59.0	41.7	18.0	8.3	3.7
6	54	66	660-670	200	39	1:1.2	115	25.4	58.8	38.0	18.3	13.4	2.1
7	41	48	680-690	150	39	1:1.1	87	16.1	63.2	22.6	21.8	9.5	3.1
8	41	47	700-710	140	36	1:1.0	83	31.6	62.2	11.6	25.7	2.5	4.0
9	33	75	650-660	174	39	1:2.0	104	Not determined		33.0	16.9	12.1	2.7
10	30	104	650-660	210	39	1:3.1	120	"	"	13.2	29.7	16.3	1.9
11	53	64	600-610	108	21	1:1.1	90	"	"	10.7	7.1	1.6	3.8
12	30	38	600-610	168	60	1:1.1	61	"	"	25.9	1.2	3.1	3.4
13	30	38	600-610	300	111	1:1.1	59	"	"	20.5	16.6	7.0	4.1

• The yield of gaseous reaction products was 70 moles (0.75 mole % calculated on silane).

2. Decomposition of chlorobenzene in hydrogen atmosphere. A mixture of chlorobenzene and hydrogen in such a ratio that the chlorobenzene concentration corresponded to its concentration in the experiments on the phenylation of dichlorosilane was fed into the reaction tube described above at 600-650°. The reaction products were condensed in a similar manner to series 1, and on completion of the run the mixture was distilled in a column with the equivalent of 26 theoretical plates to separate benzene and chlorobenzene (see Table 2).

3. Decomposition of chlorobenzene in the presence of silane. The silane was obtained by the reaction of triethoxysilane with metallic sodium at 80-85° [2] and was fed in stream of dry nitrogen (2 liters/hour) into the reaction tube at 600°. Chlorobenzene was fed from a dropping funnel. The reaction products were collected in receivers which were cooled with ice and a mixture of dry ice with acetone. The gaseous products were led through two traps filled with alkali solution. The mixture of liquid reaction products was distilled in a column with the equivalent of 26 theoretical plates two separate benzene and chlorobenzene (see No. 3, Table 2).

TABLE 2. Decomposition of Chlorobenzene

Run No.	Chlorobenzene charged, g	Hydrogen feed rate, liter/hr	Nitrogen feed rate, liter/hr	Silicon hydride charged, g	Experiment temperature, °C	Duration of run, min	Contact time, sec	Yield of liquid products, g	Yield of reaction products based on chlorobenzene taken, %	
									benzene	chlorobenzene
1	54.0	3.6	–	–	650	132	37	52.0	8.0	80.0
2	48.0	3.6	–	–	650	120	40	46.0	9.0	79.0
3	25.5	–	2.0	3.1	600	66	37	25.0	2.2	89.0

TABLE 3. Disproportionation of Dichlorosilane

Run No.	Dichlorosilane charged, g	Nitrogen feed rate, liter/hr	Temperature experiment, °C	Duration of run, min	Contact time, sec	Yield of liquid products, g	Yield of reaction products based on dichlorosilane taken, %				
							dichlorosilane	trichlorosilane	silicon tetrachloride	silicon	hydrogen chloride
1	15.6	4	650	60	42	14.9	14.3	11.0	35.7	11.6	1.9
2	39.0	4	650	150	41	36.0*	9.6	23.3	28.0	21.0	5.4

* The hydrogen content in the gaseous reaction products was 1% or 0.01 gm·mole per gm·mole of dichlorosilane.

4. Disproportionation of dichlorosilane. Dichlorosilane was fed into the reaction tube at 650° in a stream of dry nitrogen (4 liters/hour). The reaction products were condensed in three traps in series cooled to temperatures of −40°, −80°, and −180°, respectively. The gaseous reaction products were led through three traps containing and alkaline solution of known strength and were collected in a gas jar.

The condensate, collected at temperatures of −40° and −80°, was rectified and analyzed in a manner similar to the technique described above. The product collected at a temperature of −180° was treated with aqueous alkaline solution and the quantity of hydrogen liberated was determined (Table 3).

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GAS PHASE AND LIQUID PHASE OXIDATION OF n-BUTANE

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The considerable advantages of liquid phase oxidation of n-butane [1, 2] over the gas phase reaction raise the need for a comparative study of the mechanism of the process in the gas and liquid phases under comparable conditions. According to the point of view expressed by N. N. Semenov [3] the path followed by gas phase hydrocarbon oxidation processes as a function of temperature and pressure is determined by competition between free radical reactions: the isomerization of the $RO_2^{\cdot}$ radical followed by its monomolecular decomposition

$$RO_2^{\cdot} \rightarrow R'HO + R''O^{\cdot} \qquad (1)$$

and a bimolecular reaction of $RO_2^{\cdot}$ with the original hydrocarbon

$$RO_2^{\cdot} + RH \rightarrow ROOH + R^{\cdot} \qquad (2)$$

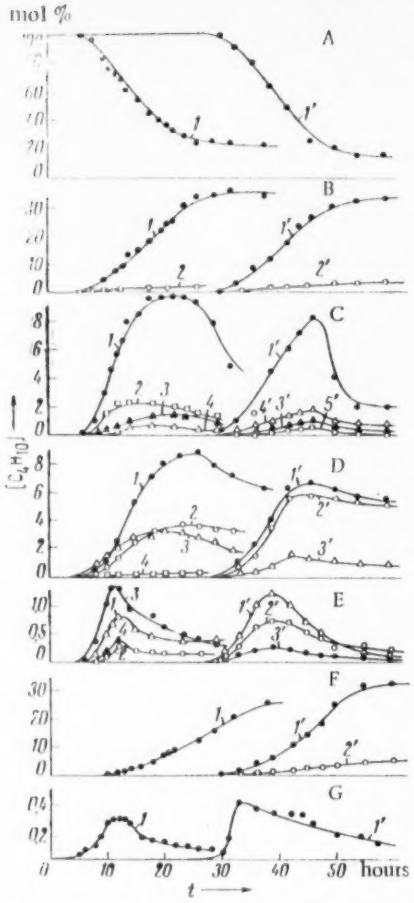
With rise in the pressure of the system the hydrocarbon density increases and reaction (2) begins to predominate. Starting from these premisses it might be presumed that the significant change in the density of a substance in passing from the gaseous to the liquid state must be the main reason for the differences in the oxidation mechanisms. However, in work recently published by us [4] we showed that in the oxidation of ethyl alcohol the change from the liquid phase to the gas phase process was accompanied by such a sharp change in the composition of the reaction products that it could not be explained within the framework of premisses regarding the competition of free radical reactions. Clearly in this case some special feature of alcohol in the liquid state, due, say, to the presence of intermolecular hydrogen bonds, plays the determining role. In the case of nonpolar compounds it is hard to envisage such a specific distinction between the substance in the gaseous and the liquid state, therefore it might be thought that the difference in the composition of the oxidation products of butane in the gas and liquid phase must probably be determined mainly by the density of the butane under the given conditions.

The oxidation of butane was carried out in an apparatus of the autoclave type described in our previous work [2], with a removable glass vessel. For liquid phase oxidation 100 ml of n-butane (which occupied practically the whole volume of the reactor when heated to the temperature of the experiment) was poured into the reactor, and, consequently, reaction in the vapors above the liquid could be ignored. For gas phase oxidation only a small quantity of butane, which developed a pressure lower than the saturated vapor at the given temperature, was poured into the reactor. Analysis of the reaction products was carried out by chemical methods and by paper chromatography [5, 6].

The kinetic curves for the consumption of butane and formation of the oxidation products at 145° and 50 atm pressure are presented in Fig. 1. The analytical results are presented in molar percent of butane which has reacted to form the given product as a proportion of the initial butane. It can be seen from Fig. 1 that the induction period for the gas phase process is considerably longer than for the liquid phase but the reaction rate on completion of the induction period is practically the same.

The main reaction products in both cases are acetic acid, methylethylketone and esters of acetic acid. However in going to the gas phase the relative yield of such substances as methyl alcohol and acetaldehyde is increased and considerable quantities of carbon monoxide and formaldehyde, which are completely absent in liquid phase oxidation also appear. Bifunctional compounds (diketones, keto-alcohols) found in the products of liquid phase oxidation of butane, completely disappear in gas phase oxidation.

In order to make a deduction as to the extent to which the composition of the oxidation products of butane under different conditions for carrying out the process varies in accordance with the hypotheses regarding competing



Kinetic curves for the consumption of n-butane and the accumulation of oxidation products at 145° and 50 atm in the liquid phase (unprimed figures) and the gas phase (primed figures). A) consumption of butane; B): 1) acetic acid; 2) formic acid; C): 1) methylethylketone; 2) diacetyl; 3) acetone; 4) acetaldehyde; 5) formaldehyde; D): 1) ethyl acetate; 2) methyl acetate; 3) butyl acetate; 4) 2-butanol-3-one acetate; E): 1) ethanol; 2) methanol; 3) butanol; 4) 2-butanol-3-one; F): 1) CO_2; 2) CO; g) peroxides.

The Maximum Rates of Accumulation of Oxidation Products of Butane formed by the Bimolecular (w_2) and the Monomolecular (w_1) Reactions of the $RO_2^{\bullet}$ Radical at 145°

Reaction products	Maximum rates of formation of reaction products in molar %			
	liquid phase		acetic acid	
	w_2	w_1	w_2	w_1
Acetic acid	1,73	0,22	0,94	0,93
Methylethylketone	1,32	—	0,60	—
Diacetyl	0,70	—	0,00	—
Methylacetate	0,30	—	0,50	—
Ethyl acetate	0,85	—	0,50	—
Butyl acetate	0,45	—	0,15	—
Keto-alcohol	0,30	—	0,05	—
Butanol	0,14	—	0,00	—
Hydroperoxide	0,15	—	0,15	—
Formic acid	—	0,10	—	0,20
Acetone	—	0,10	—	0,15
Acetaldehyde	—	0,05	—	0,40
Formaldehyde	—	0,00	—	0,06
Methanol	—	0,10	—	0,14
Ethanol	—	0,20	—	0,25
CO	—	0,00	—	0,70
CO_2	0,45	0,05	1,37	1,33
Total	6,39	0,82	4,26	4,16
w_2/w_1	7,8		1,02	

free radical reactions it is necessary to compare the rates of disappearance of butane in each of the two paths along which the $RO_2^{\bullet}$ radical reacts.

The bimolecular reaction of $RO_2^{\bullet}$ with butane can lead to the formation of hydroperoxides, methylethylketone, diacetyl, butyl alcohol, acetic acid and its esters. The products of the monomolecular decomposition of $RO_2^{\bullet}$ are aldehydes, formic acid, methyl and ethyl alcohol, CO_2 and CO. Acetic acid can be formed not only by reaction (2) but also by further oxidation of acetaldehyde which is a product of reaction (1). The same applies to carbon dioxide which can be obtained as a result of further changes undergone by the products of both reactions. Estimation of the fraction of these substances which was formed by each of the two routes in the process was carried out in the following way. By calculating w_2 as the sum of the maximum rates of accumulation of hydroperoxides, methylethylketone, diacetyl, acetates and butanol (without acetic acid and CO_2) and w_1 as the sum of the rates of accumulation of the products of the decomposition of the $RO_2^{\bullet}$ radical, we obtain the ratio $w_2/w_1 + w_2$ and we assume that this ratio also determines the fraction of acetic acid and CO_2 which are formed by the bimolecular route.

Using the data of the table in which the values of w_1 and w_2 are given for all the products of liquid phase and gas phase oxidation of butane, it is easy to assess the change in the direction of the process in going from liquid to gas phase. For the liquid phase $w_2/w_1 = 7.8$ for the gas phase 1.02, i.e., the ratio of the rates on changing the state of aggregation changes by approximately eight times altogether.

This is in agreement with the hypotheses concerning competing free radical reactions, as in the present case the concentration of butane changes by 6.5 times (from 0.39 g/cm^3 in the liquid phase to 0.06 g/cm^3 in the gas phase).

Considering these results in conjunction with the data obtained in the oxidation of ethyl alcohol [4] the deduction can be made that the difference between the mechanisms of liquid phase and gas phase oxidation of organic substances is determined not only by the external parameters of the system but also by the specific properties of the substance undergoing oxidation in the liquid phase itself. The oxidation of butane from this point of view is an example of a reaction in which the specific properties of the oxidized substance in the liquid state have practically no effect while the oxidation of ethyl alcohol is an example of a reaction the mechanism of which mainly depends on the specific properties of alcohol in the liquid state.

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INTERMOLECULAR INTERACTION OF TETRAHYDROFURANE WITH HYDROGEN CHLORIDE

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It has been previously shown by Raman spectra and vapor pressure methods that a hydrogen bond is formed between dimethyl ether and HCl, the heat of formation being $\Delta H = -7.4$ kcal/mole and the entropy $\Delta S = -28$ enthalpy units [1].

In the present work the Raman and infrared absorption spectra of the tetrahydrofurane – HCl system were studied at various temperatures and concentrations. Tetrahydrofurane has the highest dipole moment of the well-known ethers ($\mu = 1.71$ debye units)[2], therefore the formation of a stable hydrogen bond might be expected. The Raman spectra were studied on a ISP-51 spectrograph with photoelectric recording equipment. The arrangement of the apparatus for saturating tetrahydrofurane with gaseous HCl and the thermostatically controlled optical cell are shown in Fig. 1. The concentration of HCl in the solution was determined by weighing the apparatus before and after saturation. The solution was then transferred under pressure into the optical cell. IR absorption was studied on a UR-10 spectrometer. In this case the concentration of HCl was determined by direct titration.

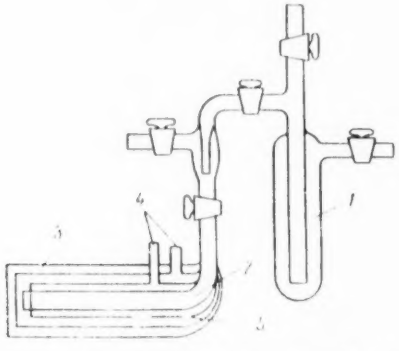
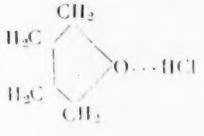


Fig. 1. General view of the apparatus for saturating tetrahydrofurane with hydrogen chloride and of the temperature-controlled cell. 1) Saturation vessel; 2) cell containing liquid under investigation; 3) Dewar jacket; 4) inlet and exit for nitrogen gas; 5) guide tube to reduce temperature gradient.

The experiments showed that the symmetrical and asymmetrical valency vibrations of the C–O–C group, the frequencies of which are about 914 and 1070 cm^{-1} respectively, are the most sensitive to interaction between molecules. When tetrahydrofurane was saturated with hydrogen chloride a reduction in the intensity of the line having a frequency of 914 cm^{-1} and the appearance of a new wide line around 870 cm^{-1} were observed in the Raman spectrum of the former (Fig. 2). The new line should be ascribed to the symmetrical valency vibration of the C–O–C goup, excited by the formation of a molecular compound



The dependence of the integrated intensity of the line with $\Delta\nu = 914$ cm^{-1} on HCl concentration is shown in Fig. 3. The ratio of the integrated line intensities I 914 cm^{-1} / I 1030 cm^{-1} is plotted along the axis of ordinates. This made it possible to compare results obtained at somewhat different settings of the spectral width of the spectrograph slit. The line with $\Delta\nu = 1030$ cm^{-1} was chosen as the "intramolecular standard" since its intensity and frequency are not very sensitive to the interaction of tetrahydrofurane with HCl (see Fig. 2). The temperature dependence of the intensity of the line with $\Delta\nu = 914$ cm^{-1} is shown in Fig. 3, from which it can be seen that variation with temperature in the tetrahydrofurane – HCl system is different than for tetrahydrofurane alone. This is explained by a shift of the equilibrium in the direction of complex formation with reduction in temperature.

When tetrahydrofurane is saturated with hydrogen chloride two new bands in the IR absorption spectrum appear at about 882 and 1052 cm^{-1} which are assigned to the symmetrical and asymmetrical valency vibrations of the

group excited by the formation of a hydrogen bond (Fig. 4). Increasing the concentration of HCl in the solution of tetrahydrofurane (n-hexane or CCl_4 was employed as the solvent) leads to an increase in the intensity of the low frequency components and a reduction in the high frequency components. Raising the temperature from 0 to 50° leads to the reverse effect. All this indicates that the new bands are associated with vibrations of the

group. An absorption band with a frequency of about 2360 cm^{-1} and a width of $\Delta\nu_{\frac{1}{2}} \approx 300$ cm^{-1}, which corresponds to vibrations of HCl molecules participating in the formation of molecular compounds, was also observed in the spectrum.

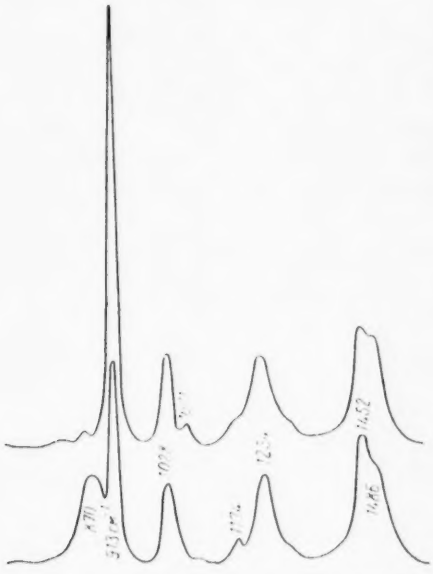


Fig. 2. Raman spectrum of tetrahydrofurane.

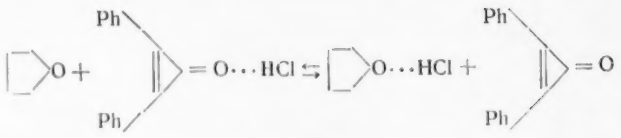
The enthalpy (ΔH), entropy (ΔS), and free energy (ΔF) changes associated with the formation of a molecular compound between tetrahydrofurane and HCl were estimated from the temperature dependence of the integral intensity of the band with $\nu = 914$ cm^{-1}. These were found to be equal to, respectively: $\Delta H = -11.5 \pm 2.5$ kcal/mole, $\Delta S = -32 \pm 6$ entropy units, $\Delta F \approx -2$ kcal/mole. It is interesting to compare the results obtained with some well-known literature data.

It can be seen from Table 1 that tetrahydrofurane forms the most stable hydrogen bond with HCl. In general ethers form more stable hydrogen bonds than ketones. This deduction follows from the fact that in the case of ethers the higher the enthalpy change the greater the frequency shift for valency vibrations into the region of lower frequencies. We will show that the strength of a hydrogen bond is assessed from the enthalpy. As regards free energy, this is a different property which determines the equilibrium constant and which depends not only on enthalpy but also on entropy. The fact that ethers form stronger hydrogen bonds than ketones with the same molecules cannot be explained by the difference in dipole-dipole interaction (since $\mu_{eth} < \mu_{ket}$).

Systems	ΔH, kcal/mole	$\Delta\nu_{X-H}$, cm^{-1}	μ, debye units	I, ev
Acetone + chloroform [4]	−4.2		2.7	9.69
+ chloroform [5]	−2.5			
+ chloroform [6]	−3.3			
+ chloroform [7]	−2.7			
+ deutero-chloroform [11]		$\nu_1 - \nu_{CD} = 0$		
+ pyrrole [9]		$\nu_0 - \nu_{NH} = -140$		
+ phenol [9]		$\nu_0 - \nu_{OH} = -200$		
Acetylchloride + HCl [10]		$\nu_0 - \nu_{HCl} = -80$	2.40	
Diphenylcyclopropenone + HCl [11]	−6.0	$\nu_0 - \nu_{HCl} = -106$	5.08	
Tetrahydrofurane + HCl	−11.6	$\nu_0 - \nu_{HCl} = -526$	1.71	
Dimethyl ether + HCl [1]	−7.4	$\nu_0 - \nu_{HCl} = -486$	1.29	10
Diethyl ether + HCl [12]		$\nu_0 - \nu_{HCl} = -435$	1.16	9.53
+ pyrrole [5]		$\nu_0 - \nu_{NH} = -178$		
+ phenol [9]		$\nu_0 - \nu_{OH} = -310$		
+ chloroform [13]	−6.02			
+ chloroform [14]	−6.0			
+ chloroform [15]	−(6-7)			
+ deutero-chloroform [8]		$\nu_1 - \nu_{CD} = -10$		

Note: ν_0) vibration frequency in gas, ν_1) vibration frequency in pure substance, ν) in solution.

Our experiments show that the reaction



goes from left to right. This obviously indicates that the formation of a hydrogen bond with an ether having a moment of 1.71 debye units is more favored than the formation of a hydrogen bond with a ketone whose moment is 5.08 debye units [11]. Let us point out that although there is a fall in entropy in this reaction it is still strongly shifted to the right, obviously on account of a reduction in enthalpy. The ionization potentials, which reflect to some extent donor capacity of ethers and ketones are similar to each other, e.g., 9.69 ev for acetone and 10 ev for dimethyl ether [16]. The explanation for the difference must be sought in the quantum nature of the hydrogen bond.

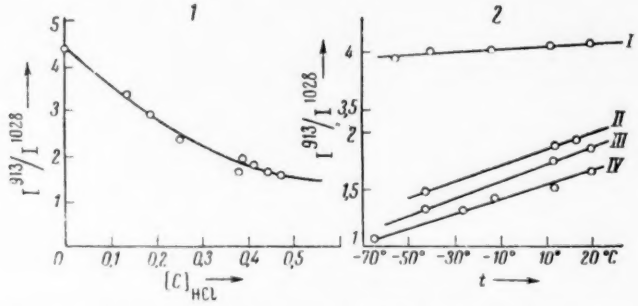


Fig. 3. Relationship between the ratio of the integrated line intensities I^{913}/I^{1028} of the Raman spectrum of tetrahydrofuran and hydrogen chloride concentration (1) (in mole fractions) and temperature (2). I) Pure tetrahydrofuran; II) tetrahydrofuran + HCl, $C_{HCl} = 0.37$; III) $C_{HCl} = 0.38$; IV) $C_{HCl} = 0.44$.

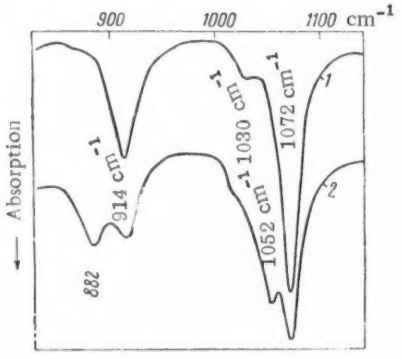
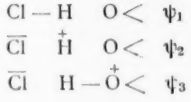


Fig. 4. IR absorption spectrum for tetrahydrofurane in CCl_4 solution (1) (C_{thf} = = 0.77 mole/liter, t = 25°) and IR absorption spectrum of the system tetrahydrofurane + HCl (2) (C_{thf} = 0.77 mole/liter, C_{HCl} = 0.54 mole/liter, t = 25°).

Many studies have been devoted to the theory of the hydrogen bond. The quantum-chemical treatment of this question is due to Coulson and Danielson [17]. In addition to the normal covalent bond (Ψ_1) and the ionic component (Ψ_2) an oxonium structure is also taken into account (Ψ_3),



so that the complete wave function has the form $\Psi = C_1\Psi_1 + C_2\Psi_2 + C_3\Psi_3$. In the normal long hydrogen bond, where the hydrogen is a long way from the oxygen, the weight of structure Ψ_3 is slight. It amounts to only a few percent. Thus a result which also appears to be the most straightforward is obtained: the normal hydrogen bond is due to van der Waals' interaction. Coulson and Danielson showed that in the case of tetrahedral sp^3 orbits the weight of the oxonium state is greater than when pure p orbits are involved. This is explained by the higher value of the superposition integral.

We suggest that the difference between ethers and ketones is associated with the weight of the oxonium structure which is considered

as a covalent component of the hydrogen bond. In the formation of a hydrogen bond not only polarity but also hybridization of the oxygen atom plays a determining role.

However, in the case of compounds of the same type, molecules with a greater dipole moment give stronger hydrogen bonds, as can be seen from a comparison of tetrahydrofurane (μ = 1.17 debye units, $\Delta H = -11.5$ kcal per mole) and dimethyl ether (μ = 1.29 debye units, $\Delta H = -7.4$ kcal/mole). The authors of some theoretical studies come to the conclusion that the oxygen of a carbonyl group must form stronger hydrogen bonds than the oxygen in an ether group [18]. This conclusion is however in contradiction with experiment.

We point out in conclusion that in order to explain the difference in the strength of the hydrogen bonds formed by ethers and ketones, it would be of interest to know their energy of affinity for a proton.

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THE CONDENSATION OF FORMALDEHYDE WITH PERFLUORO-OLEFINS – TETRAFLUOROETHYLENE, HEXAFLUOROPROPYLENE, AND TRIFLUORO-CHLOROETHYLENE

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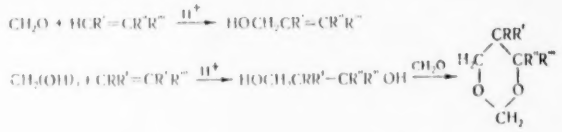
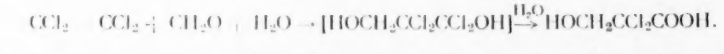
A consequence of the electrophilic character of the double bond in fluoro-olefins is, as is well-known, the exceptional ease with which they react with various nucleophilic reagents – alcohols, mercaptans, amines, organic compounds of magnesium etc. At the same time the reactions with electrophilic reagents which are typical of hydrocarbon olefins are seriously hindered and have therefore been investigated to a considerably lesser extent. In particular, to this type of reaction belongs the condensation with formaldehyde in the presence of strong acids which, in the case of ordinary olefins, leads either to unsaturated alcohols or to 1,3-glycols or their derivatives – the metadioxanes (Prins reaction):



If R'' and R''' are halogens, β-hydroxy-acids or their derivatives are formed, e.g., [1]:



In 1949 Coffman, Raasch et al., carried out the condensation of formaldehyde with tetrafluoroethylene in the presence of 80% sulfuric acid and obtained in small yield α,α-difluorohydracrylic acid, which was isolated in the form of its ethyl ester [2, 3]. In 1952, McBee et al., repeated this reaction and obtained the ethyl ester of α,α-difluoroacrylic acid with 20% yield [4].

Taking 1,2-difluoro-1,2-dichloro-ethylene, we established that in this case chlorosulfonic and fluorosulfonic acids were extremely effective catalysts for the Prins reaction and that the reaction could not be carried out in the presence of sulfuric acid at various concentrations [5]. The further study of the catalysts mentioned and their use to extend the Prins reaction to the fluorine-substituted olefin series appeared to be of interest. In the present work we report the results of an investigation of the reaction of formaldehyde with tetrafluoroethylene, hexfluoropropylene, and trifluorochloroethylene in the presence of chlorosulfonic acid.

It was found that on heating a mixture of tetrafluoroethylene, paraformaldehyde, and chlorosulfonic acid to 100° condensation occurs in accordance with the general scheme of the Prins reaction with the formation of α,α-difluorohydracrylic acid which is separated in the form of its ethyl ester. The yield of the latter was 62.6%, which was an extremely probable confirmation of the high activity of chlorosulfonic acid in comparison with sulfuric acid.

Condensation of paraformaldehyde with hexafluoropropylene in the presence of chlorosulfonic acid at 130-150° led to α-fluoro-α-trifluoromethylhydracrylic acid with a yield of 41%:

The formation of this compound is in accordance with the polarization of the double bond in hexafluoropropylene $\overset{\delta+}{CF_2} = \overset{\delta-}{CF} - CF_3$.

The double bond in trifluorochloroethylene $CF_2 = CFCl$ is polarized in such a way that the fractional negative charge is on the carbon atom of the CFCl group. This polarization is demonstrated by numerous reactions in which nucleophilic addition to $CF_2=CFCl$ occurs, by which in the final count only derivatives of fluorochloroacetic acid are formed [6-8]. It should thus be expected that the condensation of formaldehyde with trifluorochloroethylene would lead to α-fluoro-α-chlorohydracrylic acid:

$$HOCH_2^{+} + \overset{\delta-}{C}FCl = \overset{\delta+}{C}F_2 \rightarrow [HOCH_2CFClCF_2]^{+} \xrightarrow{H_2O} HOCH_2CFClCOOH.$$

This acid was in fact isolated in the form of the ethyl ester with a yield of 19.8% of theoretical. However along with this compound the ethyl ester of α,α-difluorohydracrylic acid was obtained with 30.5% yield, the formation of which cannot be explained otherwise than as the result of electrophilic attack on the CF_2 group, i.e., on the carbon atom less negatively polarized than the carbon atom of the CFCl grouping of trifluorochloroethylene.

Earlier Knunyants, Shokina and Li observed the occurrence of dual orientation in the addition of iodine chloride to trifluorochloroethylene [9]:

$$CF_2 = CFCl + Cl \rightarrow CF_2 - CFCl_2 + CF_2Cl - CFCl .$$

Whether this reaction occurs by an ionic or a free radical mechanism remains however unknown. In the case of the condensation with formaldehyde however an orientation opposite to the polarity is observed in a clearly ionic process – electrophilic addition across a multiple bond. Evidently this phenomenon may find an explanation in the competition of polar and steric factors. The effective radius of the F atom is equal to 1.25 A, and of the Cl atom to 1.58 A; thus the reaction path which is in accordance with the polarity encounters greater steric hindrance. At the same time in the case of nucleophilic addition to trifluorochloroethylene the effects of polar steric factors coincide and therefore the orientation in these reactions should be, and is strictly in one direction.

EXPERIMENTAL

Condensation of formaldehyde with tetrafluoroethylene. The ethyl ester of α,α-difluorohydroxyacrylic acid. 14.5 g (0.48 mole) of paraformaldehyde and 140 g (1.2 mole) of chlorosulfonic acid were placed in a 250 ml capacity steel autoclave. After evacuation and cooling with liquid nitrogen 35 g (0.35 mole) of tetrafluoroethylene were condensed in the autoclave, after which the mixture was shaken for seven hours at 100°. On cooling, the reaction mixture was poured over 100 g ice. The organic layer was separated and treated with soda solution until carbon dioxide stopped evolving. The substance which did not dissolve in soda was extracted with ether and rejected while the aqueous portion was added to the aqueous layer separated earlier (the reaction of this phase was strongly acidic) and continuously extracted with ether for several hours. The ether extract was dried over magnesium sulfate and the ether distilled off (under vacuum in the final stages). The α,α-difluorohydroxyacrylic acid obtained was esterified with ethyl alcohol in the presence of a catalytic quantity of chlorosulfonic acid with removal of water by azeotropic distillation with dichloroethane. 3.8 g (62.6%) of the ethyl ester of α,α-difluorohydroxyacrylic acid with a b. p. of 66-69° at 6 mm mercury was obtained. A substance was obtained by a second distillation with b. p. 69.5° at 7 mm mercury, $n^{20}D$ 1.3840, d^{20}_4 1.2612. MR found 28.57; calculated for $C_5H_8F_2O_3$ 28.75. Literature data [3]: b. p. 58-61° at 6 mm mercury, 181° at 760 mm mercury, $n^{20}D$ 1.3830. H_{act} number found 1.02; 1.03; calculated for $C_5H_8F_2O_3$ 1.00.

The amide of α,α-difluorohydroxyacrylic acid was obtained by treating the ester with a solution of ammonia in water and alcohol. M. p. 98-99° (crystallized from water).

Found %: C 28.56, 28.63; H 3.97, 4.00; F 31.39, 31.30; N 10.70, 10.70. $C_3H_5F_2NO_2$. Calculated %: C 28.81; H 4.02; F 30.38; N 10.20.

Condensation of formaldehyde with hexafluoropropylene. α-Trifluoromethyl-α-fluorohydroxyacrylic acid. A mixture of 28 g (0.186 mole) hexafluoropropylene, 10.7 g (0.36 mole) of paraformaldehyde and 75 g (0.64 mole) of chlorosulfonic acid were shaken together in a 250 ml capacity steel autoclave at 140-150° for seven hours. On cooling unreacted perfluoropropylene (11 g) was distilled off, and the reaction mixture was added to a mixture of 150 g potassium chloride and 100 ml conc. hydrochloric acid; the mixture obtained was boiled with stirring for four hours. On cooling to room temperature the precipitate was filtered off and washed with water. The filtrate was extracted continuously with ether for several hours, the extract was dried with magnesium sulfate and the ether distilled off (under vacuum in the final stages). On cooling a little dry benzene was added to the residue. 8.4 g (41.3% on the perfluoroethylene entering the reaction) of α-trifluoromethyl-α-fluorohydroxyacrylic acid, m. p. 107-108°

(crystallized from benzene) was obtained. Equivalent weight by neutralization, found 174.3; 178.1; calculated for $C_4H_4F_4O_3$ 176.1.

Found %: C 27.46, 27.21; H 2.25, 2.44; F 43.50, 43.10. $C_4H_4F_4O_3$. Calculated %: C 27.28; H 2.28; F 43.20.

Aniline salt, m. p. 164-165° (crystallized from benzene-alcohol mixture).

Found %: N 5.26, 5.35. $C_{10}H_{11}F_4O_3N$. Calculated %: N 5.20.

The ethyl ester of α-trifluoromethyl-α-fluorohydroxyacrylic acid was obtained with a yield of 61% by the esterification of the acid with ethanol in the presence of the etherate of boron trifluoride. B. p. 76.5° – 77° at 11 mm mercury, $n^{20}D$ 1.3650, d_4^{20} 1.3590. MR found 33.55; calculated 33.64.

Found %: C 35.17, 35.21; H 3.93, 3.81. $C_6H_8F_4O_3$. Calculated %: C 35.31; H 3.95.

The amide of α-trifluoromethyl-α-fluorohydroxyacrylic acid was obtained from the ethyl ester by the action of a solution ammonia in water and alcohol. M. p. 117-118° (crystallized from benzene).

Found %: F 42.72, 43.04; N 8.44, 8.32. $C_4H_5F_4O_2N$. Calculated %: F 43.44; N 8.00.

Condensation of formaldehyde with trifluorochloroethylene. A mixture of 45 g (0.39 mole) of trifluorochloroethylene 14.2 (0.48 mole) of paraformaldehyde and 148 g (1.27 moles) of chlorosulfonic acid were shaken together for 7 hours. On cooling the reaction mixture was treated as in the case of tetrafluoroethylene. The following were obtained by fractionation:

1. The ethyl ester of α,α-difluorohydroxyacrylic acid. 18.2 g (30.5%), b. p. 64-64.5° at 5 mm mercury, $n^{20}D$ 1.3862. The amide of α,α-difluorohydroxyacrylic acid having a melting point and a melting point when the sample was mixed with a known sample of 98-99°.

2. The ethyl ester of α-fluoro-α-chlorohydroxyacrylic acid, 13 g (19.8%), b. p. 82° at 6 mm mercury, $n^{20}D$ 1.4249, d^{20}_4 1.3032. MR found 33.47; calculated 33.48.

Found %: C 35.41, 35.52; H 4.78, 4.78; F 11.59, 11.91. $C_5H_8FClO_3$.
Calculated %: C 35.22; H 4.73; F 11.14.

The amide of α-fluoro-α-chlorohydroxyacrylic acid was obtained from the ethyl ester by the action of a solution of ammonia in water and alcohol. M. p. 101-102° (crystallized from dichloroethane).

Found %: C 25.57, 25.52; H 3.80, 3.70; F 14.31, 14.72. $C_3H_5FClO_3$.
Calculated %: C 25.46; H 3.56; F 13.43.

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THE "THERMAL" REARRANGEMENT OF HYDRAZO-COMPOUNDS

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On the basis of earlier work [1] it might be supposed that hydrazo-compounds breakdown when heated in an inert atmosphere to form disproportionation products exclusively. Somewhat later Wieland [2] showed that in the cases of 4-methyl-, 4-methyl-4-methoxy-, and 4-methyl-4-chlorohydrazobenzene the corresponding semidines must also be taken into consideration. According to our data [3] the hydrazo-compounds of a series of naphthalenes, in particular 2,2'-hydrazonaphthalene, on moderate heating (100°) in inert solvents mainly forms rearrangement products. Finally these products were confirmed qualitatively after heating (150°) hydrazobenzene and 2,2'-dimethylhydrazobenzene for 20 days [4].

TABLE 1

Expt. No.	Hydrazo-compound	Temp., °C	Heating time, hours	Obtained, percent of theoretical				Total substances, % of theoretical
				o-semidines	p-semidines	anilines	azo-compounds	
1	Hydrazobenzene	140-145	120	16.7	12.5	31.5	33.4	94.1
2	2,2'-dimethylhydrazobenzene	140-145	120	8.3	13.1	36.0	38.0	95.4
3	4-Methylhydrazobenzene	140-145	116	18.6	8.1	33.5	35.6	95.8
4	4,4'-Dimethylhydrazobenzene	140-145	100	15.5	–	38.0	38.2	91.7
5	4-Chlorohydrazobenzene	140-145	20	–	–	45.2	47.5	92.7
6	4-Bromohydrazobenzene	110	16	–	–	46.5	50.3	96.8
7	2,2'-Methoxyhydrazobenzene	120-125	26	16.0	9.2	28.5	40.2	93.9

TABLE 2

Expt. No.	Hydrazo-naphthalene	Temp., °C	Solvent	Obtained, percent of theoretical							Total substances, % of theor.
				o-diamines	imines	p-diamines	o-semidines	p-semidines	naphthylamines	azo-compound	
1	1,1'	85	abs. alcohol	4.4	26.1	26.1	6.9	7.0	12.7	8.5	91.7
2	1,1'	100	benzene	6.6	8.5	1.0	9.4	18.4	23.5	23.0	90.4
3	1,1'	145	–	4.7	10.2	1.5	13.6	23.2	19.6	19.2	91.0
4	2,2'	100	abs. alcohol	74.9	18.5	–	–	–	–	–	93.4
5	2,2'	160	benzene	70.0	23.0	–	–	–	–	–	93.0
6	2,2'	140	–	65.1	28.8	–	–	–	–	–	93.9
7	1,2'	100	abs. alcohol	30.4	56.4	–	–	–	1.0	1.5	89.3
8	1,2'	145	–	29.0	38.0	–	–	12.2	4.2	5.0	88.4

It is now possible to make a more detailed report on the results of the conversion of a series of hydrazo-compounds on heating. The optimum reaction conditions for individual members of the series are far from being the same; thus, for example, hydrazobenzene and 2,2'-dimethylhydrazobenzene breakdown completely in 120 hr at 140-145°, the balance on the substances produced in the reaction being as high as 95% of theoretical; if the temperature is raised to 150°, some tar formation is observed in the reaction mixture. In the case of 4,4'-dichloro- or

4-bromohydrazobenzene more gentle conditions are necessary, as the mixture rapidly darkens and cokes up at 140°. The complete decomposition of the hydrazo-compounds of the naphthalene series takes only several minutes in the range 140-150°.

The results of the conversion of a series of hydrazo-compounds by heating are presented in Tables 1 and 2.

The compounds investigated can be broken down into three groups. First, hydrazo-compounds which form almost exclusively disproportionation products; the quantities of semidines in these cases do not amount to 1% of theoretical; 4-chloro-, 4,4'-dichloro- and 4-bromohydrazobenzene belong to this group.

The majority of the hydrazo-compounds of the benzene series belong to the second group; the quantity of rearrangement products sometimes exceeds 25% of theoretical. These are o- and p-semidines,* with one or other isomer predominating in individual cases. It is of interest that in the rearrangement of 4-methylhydrazobenzene not only 2-amino-5-methyldiphenylamine but also the second possible o-semidine (2-amino-4'-methyldiphenylamine), which was not observed by Jacobson [5] in the rearrangement under acidic conditions, are obtained.

The hydrazo-compounds of the naphthalene series form the third group. The rearrangement of 1,1-hydrazonaphthalene takes place in the most complex manner. A very significant portion of the hydrazo-compound undergoes disproportionation but apart from 1,1'-azonaphthalene and α-napthylamine the following substances have been determined quantitatively: 1) 1,1'-diamino-2,2'-dinaphthyl, 2) the corresponding carbazol derivative 2,2'-dinaphtho-1,1'-imine, 3) 4,4'-diamino-1,1'-dinaphthyl, 4) 1-amino-2,1'-dinaphthylamine, 5) 4-amino-1,1'-dinaphthylamine. The position becomes even more complex if consideration is given to the fact that rearrangement in alcohol (experiment 1), the results of which are reminiscent of the normal process carried out by the action of acids, is very different from rearrangement in benzene (experiment 2) or without a solvent (experiment 3); whereas in alcohol mainly diamines and 2,2'-dinaphtho-1,1'-imine, corresponding to the 1,1'-diamine, are obtained; in benzene ,or without a solvent,semidines predominate.

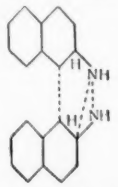
The rearrangement products of 1,2'-hydrazo-naphthalene correspond to a mixed hydrazo-compound only. In an alcoholic medium the o-diamine and, in very large quantities (56.4%), the corresponding carbazol derivative are obtained; in the absence of a solvent 4-amino-1,2'-dinaphthylamine is also formed. Disproportionation is negligible. The behavior of 2,2'-hydrazonaphthalene on heating is more uniform, in which case only the o-diamine (75-65%) and 1,1'-dinaphtho-2,2'-imine (18.5-28.8%) are obtained irrespective of the conditions. It is possible to demonstrate that 2,2'-hydrazonaphthalene is capable of rearrangement even at room temperature: after standing for about a year under freshly distilled ethyl alcohol, which filled the whole apparatus, very fine crystals of the hydrazo-compound broke down completely. After separation of the crystalline hydrazo-compound and treating the alcoholic solution with large quantities of mercurous oxide (to oxidize any hydrazo-compound) pure 2,2'-diamino-1,1'-dinaphthyl to the extent of about 16% of theoretical was separated; the quantity of 2,2'-azonaphthalene was 76% of theoretical.

Thus, as a result of the decomposition of hydrazo-compounds on heating,azo-compounds and anilines are obtained in the first place; these are products of the bimolecular oxidation-reduction reaction:

$$2RNH-NHR \rightarrow RN=NR + 2RNH_2.$$

The second group of substances are the o- and p-semidines. The formation of these compounds can be envisaged as the result of the reaction of radicals occurring on the rupture of the N − N bond of the hydrazo-compound [4] under conditions which are not at variance with the accepted ideas of the rearrangement being a intramolecular process.

The third group are substances with new C−C and C−N bonds − diamines and dinaphthoimines. It is an important point that none of the three isomeric dinaphthoimines, which are sometimes formed in large quantities, can be obtained from previously prepared diaminonaphthyls, as more drastic conditions are required for this; this has been confirmed in an appropriate manner for all three isomers. Consequently, they are formed at the instant the rearrangement occurs. The following, for example, is conceivable as an intermediate state:



* It is clear that only the o-semidine was obtained in experiment No. 4 (Table 1).

where the linkage between the nitrogen atoms has not finally broken and new linkages have not been finally established.

In conclusion the statement may be made that thermal rearrangement has much in common with the rearrangement of hydrazo-compounds under acid conditions; but whereas in the former case the hydrazo molecule acquires the necessary lability by heating, in the second case the addition of a proton is necessary for rearrangement to be effected, after which the monoprotonized [6] hydrazo-compound is capable of undergoing change in the three directions mentioned.

EXPERIMENTAL

Hydrazo-compounds of the benzene series. About 0.02 mole of the hydrazo-compound was heated in a sealed tube under nitrogen, after which the contents of the tube were extracted with ether or a mixture or ether with petroleum ether and shaken together with dilute sulfuric acid (1.1-1.2 g H_2SO_4 in 30-50 ml of water). Aniline sulfates, with the exception of the sulfates of p-chloro- and p-bromoaniline, remained in solution and the p-semidine sulfates crystallized out. To purify them they were reprecipitated or converted to the free bases, yielding almost pure substances. In determining the yields of p-semidines their solubility under the conditions of separation was allowed for. In 100 ml water acidified with 4-5 drops of H_2SO_4 about 0.03-0.04 g of 4-aminodiphenylamine dissolves at 0°, about 0.16 g of 4-amino-5,2'-dimethylphenylamine, and 0.5-0.6 g of 4-amino-5,2'-dimethoxydiphenylamine (the m. p. of this base is 108°); the solubility of 4-amino-4'-diphenylamine sulfate is negligible. The main quantities of o-semidines together with azo-compounds were in the ethereal solutions, and a small portion in the acid aqueous solutions together with the anilines from which they could be extracted completely with ether, after which the o-semidines were again converted to salts by shaking the ethereal solutions with hydrochloric acid; in the case of 2-aminodiphenylamine 10% hydrochloric acid was adequate, but for 2-amino-4'-methyl- or 2-amino-5,4'-dimethylphenylamine it was necessary to use 20-25% acid. The anilines were as usual [7] twice steam-distilled and determined by diazotization. It should be pointed out that neither benzidines nor diphenylines were found; they could not be detected either with the p-semidines (employing the very low solubility of dibenzoylbenzidines in, say, acetone) or in the residues after the steam distillation of the anilines [8].

1,1'-Hydrazonaphthalene. 1) 0.0025 mole was heated for three hours in ten ml of absolute alcohol. After removal of the alcohol under vacuum the residue was dissolved in benzene, to which ether was added, and shaken together with 0.5 N HCl (40 ml). The residue of hydrochlorides of the 4,4'-diamine and the p-semidine were separated and converted to the bases by treatment with a small excess of NaOH in aqueous (85%) methyl alcohol, almost pure 4,4'-diamino-1,1'-dinaphthyl being completely precipitated. On dilution of the solution with water a residue separated which was treated with benzoyl chloride in the presence of soda, filtered off and washed with ether, yielding almost pure benzoyl p-semidine with traces of dibenzoyl 4,4'-diamine (insoluble in acetone). α-Naphthylamine in the hydrochloric acid solution was determined by diazotization. The benzene-ether solution was shaken with 30% sulfuric acid (10-15 ml) yielding in the presence of the o-semidine an insoluble sulfate which was converted to pure 1-amino-2,1'-dinaphthylamine on treatment with alkali. The sulfuric acid solution was diluted with water and neutralized to separate 1,1'-diamino-2,2'-dinaphthyl. The benzene-ether solution was evaporated, the residue was boiled with methyl alcohol (8-10 ml), cooled and the imine solution was separated from the azo-compound. On removing the alcohol, imine remained which was contaminated with a trace of the azo-compound which was removed by a second treatment in the imine with boiling petroleum ether; the 1,1'-azonaphthalene was recrystallized from ethyl alcohol in order to purify it.

2) 0.0042 mole was heated for six hours in 40 ml benzene. Treatment was similar to the preceding one, but the difference in the results is very great; the quantity of the 4,4'-diamine was insignificant, but on the other hand the quantities of the o- and p-semidines increased.

3) 0.0025 mole was heated in a sealed tube; within 2-3 minutes the hydrazo-compound began to melt, the mixture reddened, expanded and rapidly settled on the bottom of the tube. On unsealing the tube, the mixture was dissolved in benzene and processed as in the preceding case.

1,2'-Hydrazonaphthalene.* 1) 0.0031 mole was heated for three hours at 100° in 10 ml abs. alcohol. After removal of the alcohol it was treated with 10 ml of benzene and the insoluble portion was washed with petroleum ether; the residue was pure 1,2'-dinaphtho-2,1'-imine. The hydrocarbon solution was shaken together first with 0.5 N HCl (40 ml) and then with 2.0 N HCl (15 ml). The slight tarry precipitate did not give a reaction either for the para- or the ortho-semidine. The first solution was made alkaline with soda and was treated with benzoyl

chloride; after washing with ether on the filter almost pure dibenzoyl-o-diaminodinaphthyl remained. After removing the ether a small quantity of a precipitate melting in the range 100-110° (the dibenzoyl derivatives of α- and β-naphthylamines) was obtained. When the solution in 2 N HCl was made alkaline the o-diamine was precipitated. The hydrocarbon solution was shaken up with 4 N HCl to purify it, washed with water, the solvent was stripped off and the residue boiled with a mixture of benzene and petroleum ether in a ration of 1:2 (10 ml); the residue was the pure imine.

2) 0.0031 mole of the hydrazo-compound was heated in a sealed tube for 5 minutes under nitrogen. The mixture was dissolved in benzene and the procedure was generally as before. On shaking with 0.5 N HCl in this case a precipitate of 4-amino-1,2'-dinaphthylamine hydrochloride was formed.

2,2'-hydrazonaphthalene.* 1) 0.0035 mole in 20 ml of abs. alcohol was heated for three hours. The residue contained the pure o-diamine which was washed with petroleum ether. The solvent was removed and the residue dissolved in ether, shaken with 3 N HCl, and made alkaline causing an additional quantity of the o-diamine to separate. The ethereal solution contained 1,1'-dinaphtho-2,2'-imine contaminated with 2,2'-azonaphthalene; these substances are easily separated with the aid of methyl alcohol in which the azo-compound is not very soluble.

2) 0.0035 mole was heated for three hours in 50 ml of benzene. The separation of the reaction products was similar to that described under experiment No. 1.

3) 0.0054 mole of the hydrazo-compound was heated for five minutes in a sealed tube; the glassy mass formed was extracted with ether to separate a portion of the o-diamine. After this the procedure was as indicated above.

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* The original 1,2'-hydrazonaphthalene contained about 6% 1,2'-azonaphthalene, while the 2,2'-isomer contained about 2% 2,2'-azonaphthalene.

THE TRI-p-AMINOTRIPHENYLOXONIUM CATION AS A STRUCTURAL ANALOG OF PARAFUCHSINE

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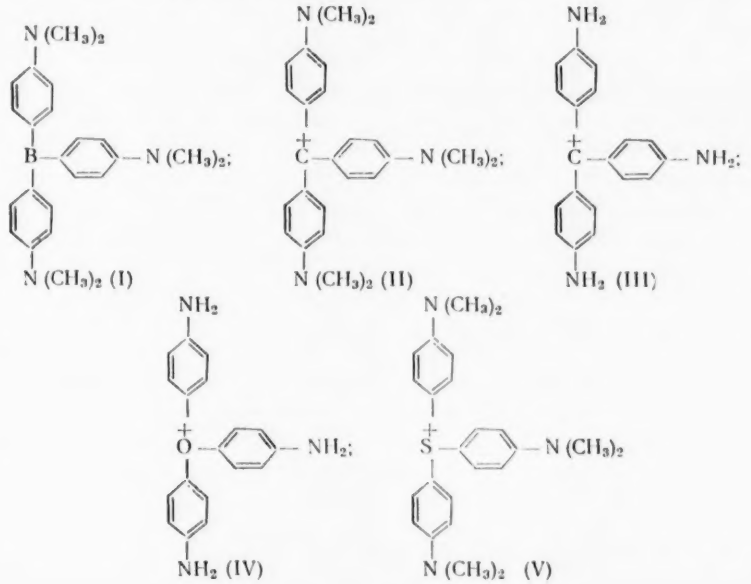
In a previous work [1] we described the nitration of a series of onium compounds including triphenyloxonium salts which we obtained previously [2]. Unlike other aromatic onium compounds which display an absolutely clearly defined meta-orientation for electrophilic substitution, triphenyloxonium salts are nitrated exclusively in the para-position.

In the present article we describe the reduction of tri-p-triphenyloxonium borofluoride to the corresponding amino-derivative and some properties of the latter. The reduction was carried out under the usual conditions with tin and hydrochloric acid. The tri-p-aminotriphenyloxonium chloride obtained in this reaction was converted by double decomposition reactions into other salts of this cation – the iodide, the double salt of the iodide, the double salt of the iodide with mercury iodide and the chloroplatinate. None of these salts has a sharp melting point but gradually carbonizes without melting on heating at 150-200°.

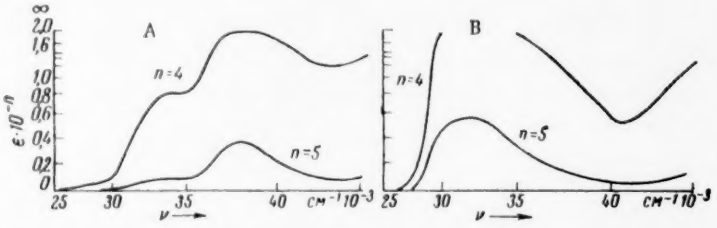
Under the influence of the oxonium oxygen atom the basic properties of the amino group in tri-p-aminotriphenyloxonium salts are markedly weakened. These amino groups only diazotize under conditions for the diazotization of weakly basic amines, e.g., when acted upon by nitrosylsulfuric acid. The diazo compound obtained couples with β-naphthol but on treatment with sodium iodide solution exchanges the diazo group for iodine.

On diazotization under the normal conditions the salts of tri-p-aminophenyloxonium are decomposed by the excess of sodium nitrite.

The tri-p-aminophenyloxonium cation is a structural analog of the parafuchsine anion, but unlike the latter it is colorless. It is interesting to compare the following series of compounds:



Of these only parafuchsine and crystal violet have an intense coloration. The remaining compounds absorb only in the ultraviolet region of the spectrum: $[p\text{-}(CH_3)_2NC_6H_4]_3C^+$ has a λ_{max} of 589 mμ ($\log \epsilon_{max} = 4.92$) [3], $[p\text{-}NH_2C_6H_4]_3C^+$ has a λ_{max} of 551 mμ ($\log \epsilon_{max} = 4.97$) [3], $[p\text{-}(CH_3)_2NC_6H_4]_3B$ absorbs in the u.v. region [4], $[p\text{-}(CH_3)_2NC_6H_4]_3S^+$ has a λ_{max} of 315 mμ ($\log \epsilon_{max} = 4.72$),* $[p\text{-}NH_2C_6H_4]_3O^+$ has a λ_{max} of 263 mμ ($\log \epsilon_{max} = 4.56$),* and 292 mμ ($\log \epsilon_{max} = 3.85$).



The ultraviolet absorption spectrum of tri-p-aminotriphenyloxonium iodide (A) and tris-(p-dimethylaminophenyl)-sulfonium chloride (B).

Thus for the intense absorption of light in the visible region characteristic of dyes in structures of the following type

where A is an auxochromic group and E is an atom of one of the elements from B to O (and sulfur), two conditions are essential.

First, E must have an electron deficit, as in B and C (a pair of electons missing to complete the octet). At the same time the possibility of extending the octet occurring in the case of sulfur does not alter the fact that a deficit is present.

Secondly, E must have the positive charge of the cation which is concentrated between E and the auxochromic groups.

It is insufficient for the occurence of color for one of these conditions to be satisfied on its own, a combination of both is essential.

EXPERIMENTAL

Salts of tri-p-aminotriphenyloxonium. a) The chloride. A mixture of 2.74 g (6 millimoles) of tri-p-aminotriphenyloxonium borofluoride, 6.85 g (0.06 g-atoms) of metallic tin and 41 ml of conc. HCl was heated under reflux until the tin dissolved completely, and was then diluted with 900 ml of water. Hydrogen sulfide was passed through the solution obtained warmed to 60° until the tin sulfides were completely precipitated. The precipitate was filtered off and washed with water, and the filtrate was evaporated to dryness. The residue – the hydrochloride of tri-p-aminotriphenyloxonium chloride – was reprecipitated from methanol with abs. ether. The yield of the salt was 2.1 g (78% of theoretical). The salt was a white powder soluble in water and methanol and sparingly soluble in acetone and ether. On heating the salt carbonizes without melting in the range 160-175°.

Found %: N 8.58. $C_{18}H_{21}N_3OCl_4$. Calculated %: N. 8.64.

By adding aqueous solutions of inorganic salts to an aqueous solution of tri-p-aminotriphenyloxonium other salts of this cation are obtained.

b) The iodide. A colorless amorphous substance, moderately soluble in acetone, sparingly soluble in cold water, insoluble in ether. On heating it carbonized without melting in the range 180-200°. The salt was purified by recrystallization from water.

Found %: C 51.28, 51.13; H 4.42, 4.29. $C_{18}H_{18}N_3OI$. Calculated %: C 51.58; H 4.32.

c) The double salt of the iodide with mercury iodide. A pale yellow fine crystalline substance, soluble in acetone, sparingly soluble in water, insoluble in ether. On heating the salt carbonizes without melting in the range 200-230°.

Found %: C 33.70; H 2.93; I 39.00. $C_{36}H_{36}N_6O_2HgI_4$. Calculated %: C 33.42; H 2.87; I 39.24.

d) The chloroplatinate. The salt is a cream colored powder, sparingly soluble in water, acetone, alcohol, nitromethane, soluble in dilute hydrochloric acid. On heating it carbonizes without melting in the range 200-250°.

Found %: N 5.76, 5.67. $C_{18}H_{19}N_3OPtCl_6$. Calculated %: N 5.99.

Salts of tri-p-iodotriphenyloxonium. a) The tri-iodide. 0.3 g (0.66 millimole) of tri-p-aminotriphenyloxonium chloride was added gradually with cooling to a solution of 0.2 g (2.6 millimoles) of $NaNO_2$ in 4 ml of conc. H_2SO_4 (d = 1.84). The clear solution of the diazonium salt obtained was poured into 15 ml of ice water and then to this was added conc. aqueous solution of NaI until the tri-p-iodotriphenyloxonium tri-iodide had been precipitated completely. The yield of this was 0.6 g (87% of theoretical). After reprecipitation from acetone with abs. ether the salt was in the form of dark red crystals with a decomposition temperature of 180-181°, highly soluble in acetone and insoluble in water and ether.

Found %: C 21.61, 21.48; H 1.18, 1.28; Hal 74.58, 74.96. $C_{18}H_{12}OI_4$. Calculated %: C 21.50; H 1.20 Hal 75.71.

b) The iodide. Obtained by double reprecipitation from acetone with ether saturated with sulfur dioxide. The salt had a decomposition temperature of 163-164°, was soluble in cold water, insoluble in ether and hydrocarbons. It crystallized with one molecule of water.

Found %: C 27.96, 28.45; H 1.70, 1.94; Hal 66.44, 66.40. $C_{18}H_{14}O_2I_4$. Calculated %: C 28.08; H 1.83; Hal 65.93.

The reaction of tri-p-aminotriphenyloxonium chloride with $NaNO_2$ in hydrochloric acid. A solution of 1 g (2.3 millimole) of tri-p-aminotriphenyloxonium chloride in 10 ml of conc. HCl was treated with a saturated solution of 2 g (30 millimoles) of $NaNO_2$ in water and then with an excess of a conc. solution of sodium iodide. The precipitate formed was extracted with ether, the ethereal solution was washed with an aqueous solution of Na_2SO_3 and dried over $CaCl_2$. The residue from the evaporation of the ether was heated under reflux with 8 ml of conc. HCl and 1.6 g of metallic tin until the latter dissolved. The undissolved residue was filtered off, washed with water and dried. This was p,p'-di-iodo-diphenyl ether. The yield of this was 0.45 g (67% of theoretical). M. p. 138-139° (after recrystallization from alcohol).

According to literature data [5] the m. p. of p,p'-di-iodo-diphenyl ether is 139°.

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THE LEAD SELINITE – LEAD OXIDE SYSTEM

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When the reaction between lead selenide and oxygen was studied [1], it was shown that at 500-600° lead selenite is the only oxidation product. At higher temperatures of the oxidation (700-900°) some crystalline phases were observed which structurally resembled the oxyselenites $2PbO \cdot PbSeO_3$ and $4PbO \cdot PbSeO_3$. These compounds and lead oxide are found among the products of thermal decomposition of lead selenite [2]. We studied the system $PbSeO_3$-PbO by thermal and x-ray phase analysis in order to determine more exactly the structure and limits of existence for lead oxyselenites.

To prepare the mixtures we used analytically pure (a.p.) yellow lead oxide and lead selenite prepared from selenious acid (a.p.) and lead nitrate (a.p.) [3]. The $PbSeO_3$ used as starting material was analyzed for lead content by complexometric titration with an indicator 1-(2-pyridylazo)-2-resorcin [4], and selenium iodometrically [5]. The positions and relative intensities of lines on the x-ray photograph of the initial lead selenite agreed well with literature data [3, 6].

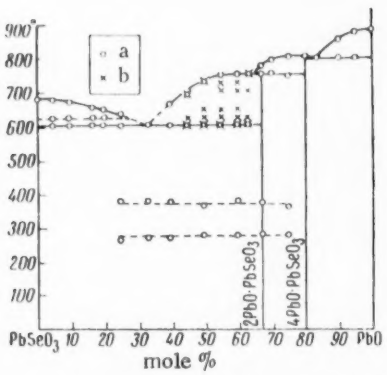

Fig. 1. System $PbSeO_3$-PbO. a) Heating rate 10-12 deg/min, b) heating rate 5-6 deg/min.

Samples for the thermal analysis were prepared by tempering of carefully pulverized and mixed components in evacuated quartz ampules. The x-ray phase and thermal analyses of some samples obtained from different tempering periods showed, that under our conditions of obtaining equilibrium mixtures containing less than 70 mole% PbO, it was sufficient to temper for 20 hr at 560-570°; for mixtures with a higher PbO content, 40 hr of tempering at 630-650° were required.* We did not prepare samples by fusion of the components, because lead selenite on fusion decomposes and releases selenium dioxide [2].

Differential thermal analysis was done on a N. S. Kurnakov PK 52 pyrometer with platinum-platinorhodium thermoelements. The temperature was determined with ± 5° accuracy. Aluminum oxide was used as a standard. The samples to be tested were mixed in platinum crucibles. The usual sample weight was 0.8 g. Only heating curves were recorded because of the strong supercooling of melts and changes in composition during the fusion. The average heating rate was 10-12 deg/min, and in some separate cases 5-6 deg/min. Chemical analysis of some samples heated to full fusion at a rate of 5-6 deg/min and cooled rapidly showed, that the composition of the mixtures changed less than 1%.

The x-ray photographs were obtained by the powder method using Fe-K emission in RKD cameras with 57.3 mm diameter. For high temperature, x-ray exposure camera "Inikam" [7] with 190.05 mm diameter was used. In all cases the substance was put into "pyrex" glass capillaries. The line intensities on the x-ray photographs were estimated visually by a five mark scale.

Figure 1 shows a diagram of the composition of the system, based on thermal and x-ray phase analyses of the tempered mixtures. Results of x-ray phase analysis of tempered mixtures are given in Fig. 2.

* At higher temperatures the substances strongly erode the quartz.

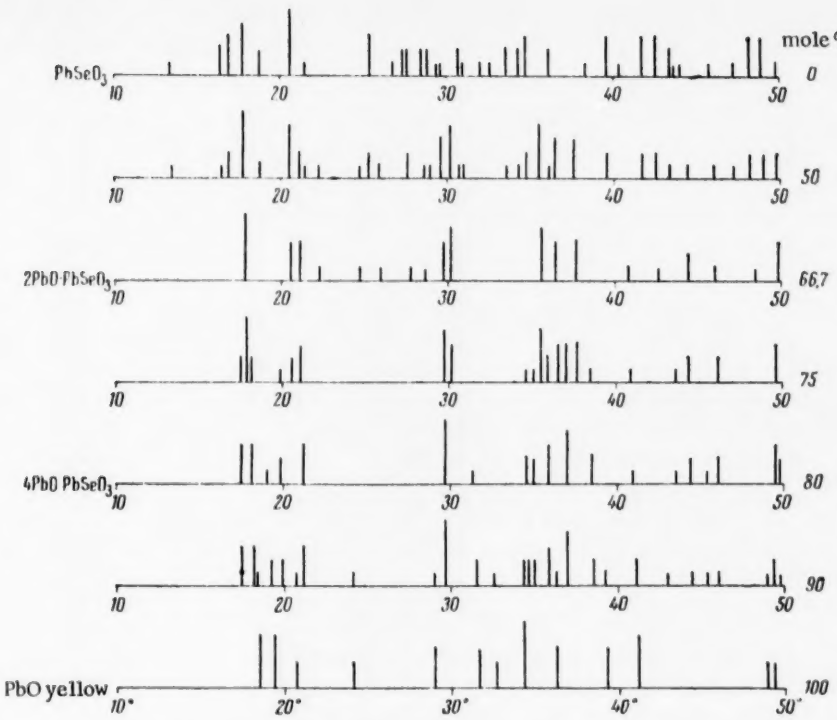

Fig. 2. Line diagrams of tempered mixtures in the system $PbSeO_3$-PbO.

We found the melting points of the components $PbSeO_3$ and PbO to be 680 and 885°, respectively. Two compounds were discovered in the system – oxyselenites of the composition $2PbO \cdot PbSeO_3$ and $4PbO \cdot PbSeO_3$.

At 755° oxyselenite $2PbO \cdot PbSeO_3$ fused and decomposed: $2PbO \cdot PbSeO_3 \rightleftharpoons$ fusion + $4PbO \cdot PbSeO_3$, and with lead selenite it formed a eutectic mixture at 605° and 33.3 mole % PbO. Congruently oxyselenite $4PbO \cdot PbSeO_3$ melts at 805° and formed a eutectic mixture with lead oxide (800°, 83.3 mole % lead oxide).

During thermal analysis in addition to the effects relating to the decomposition or fusion of the phases described above, a number of effects was observed, which could not be interpreted unequivocally. Thus, in the 45-63 mole % region when lead oxide was heated at a rate of 5-6 deg/min, a number of endothermic effects (625, 650, and 710°) is manifested, which are absent or marked by only slight inflections on differential curves at a heating rate of 10-12 deg/min. In addition, when the heating is slow, the temperatures of final fusion for mixtures containing 55 and 60 mole % PbO are lowered from 750 and 755°, respectively, to 730°. The eutectic effect is manifested (605°) on thermograms of all samples, regardless of the heating rate. It was not possible to explain the nature of these effects by comparing the peak heights on differential records and visual observations. X-ray phases: studies on tempered samples of composition 1:1 showed, that they consist only of two phases: $PbSeO_3$ and $2PbO \cdot PbSeO_3$. It was impossible to apply high-temperature x-ray exposure, because we did not succeed in securing materials for the capillaries which would not react with the substances at temperature above 600°. It is possible that the thermal effects described above were caused by the formation and conversions of the unstable oxyselenite $PbSeO_3 \cdot PbO$.

Furthermore, thermograms of mixtures containing from 5 to 20 mole % lead oxide show not only the eutectic effect, but an endothermic effect at 625°, which is absent from thermograms of pure lead selenite. The effect is reversible. On a Debye crystallogram of a sample composed of 95 mole % $PbSeO_3$ and 5 mole % PbO tempered from 640°, there are some lines in addition to the basic ones for lead selenite, which do not belong to $PbSeO_3$ $2PbO \cdot PbSeO_3$. The possibility is not excluded, that the effect is related to the fusion of the eutectic of our assumed compound $PbSeO_3 \cdot PbO$ with lead selenite.

The not always reproducible effects at 275 ± 10° and 370 ± 10° are recorded on thermograms of mixtures containing 25-75 mole % lead oxide. In order to determine the nature of these effects we prepared x-ray photographs

of a tempered mixture of 1:1 composition and oxyselenite $2PbO \cdot PbSeO_3$ at 20, 320, and 450°. All three x-ray photographs are identical. Thus, the recorded changes are not connected with the formation and decomposition of new crystalline phases, and possibly relate to some second-order conversions of oxyselenite $2PbO \cdot PbSeO_3$.

X-ray phase analysis of oxyselenites obtained showed, that they are structurally identical with crystalline phases found earlier [1] in the oxidation products of lead selenide. $2PbO \cdot PbSeO_3$ crystallizes in tetragonal lattices with the following parameters of the space centered basic cell: a) = 3.92 kX, b) = 5.37 kX; $4PbO \cdot PbSeO_3$ – rhombic with parameters of the space centered basic cell: a) = 3.92 kX, b) = 3.73 kX, c) = 5.72 kX.

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THE USE OF SPECTROPHOTOMETRY FOR THE STUDY OF COMPOSITION AND STRUCTURE OF CHLORIDE COMPLEXES OF COBALT

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In the absorption spectrum of complex ions the bands of crystalline fields are directly connected with the structure of ligand fields. This made it possible to obtain, on the basis of spectrophotometric measurements, significant information about the structure, stability, and composition of complex molecules in liquid media. In contrast to liquid media, the connection between composition and structure of crystalline substances is not direct. The use of spectrophotometry for physicochemical analysis even in that case can nevertheless illustrate the composition and structure of complex compounds. Absorption spectra of anhydrous $CoCl_2$ and complexes containing the ion $[CoCl_4]^{2-}$ have been studied many times [1-6]. An account of x-ray structure data leads to the conclusion [4-6] that the absorption band with maxima at 530 and 580 mμ belongs to the octahedral ion $[CoCl_6]^{4-}$, and the band with maxima at 412, 450, 535, 625, 660, and 685 mμ is related to the existence of tetrahedral ions $[CoCl_4]^{2-}$.

We obtained absorption spectra of crystalline alloys in systems of anhydrous $CoCl_2$ and chlorides of alkali metals.

The substance or mixture of substances in the molten state was deposited on the walls of a sealed quartz test tube in a thin layer, and the absorption of the thin polycrystalline film thus obtained was measured on an SF-4 spectrophotometer. Figures 1 to 4 give the experimental data.

Figure 1 represents absorption spectra of alloys in systems $CoCl_2$–CsCl (a) and $CoCl_2$–RbCl (b). The curve 1a is the visible region of the $CoCl_2$ absorption band, which compound has the octahedral structure. There is a maximum at 535 and 590 mμ. The absorption of the alloy $CoCl_2$ and CsCl with a molar ratio of 1:1 is represented by curve 3a. It can be seen that the curve retains the character of the octahedral band, but acquires a right arm. It was assumed that this was due to insufficient accuracy in the composition stoichiometry, causing the appearance of traces of strongly absorbing tetrahedral complexes. Actually, an alloy with molar ratio of CsCl to $CoCl_2$ equal to 0.9 does not show the right arm on the absorption chart (curve 2a). Thus it is likely that when CsCl and $CoCl_2$ are alloyed in a ratio of 1:1 an octahedral complex $CsCoCl_3$ is formed. This is a blue compound which solidifies into needles and does not hydrate in air.

The curve 4a represents the absorption spectrum of the alloy CsCl with $CoCl_2$ in a ratio of 2:1. The absorption spectrum fully coincides with the absorption chart characteristic of the tetrahedral complex Cs_2CoCl_4 [4-6]. The compound obtained is indefinitely stable in air. Alloys CsCl with $CoCl_2$ with higher molar portions of CsCl retain the spectral structure characteristic of tetrahedral complexes (illustrated by curve 5a for alloy with ratio 326). The system RbCl–$CoCl_2$ is analogous only as far as studied. It should only be added, that the absorption band of the alloy RbCl and $CoCl_2$ in ratio 1:1 has no tetrahedral right arm. The blue, needle-like crystals of $RbCoCl_3$ are stable in air for long periods, after which they are converted to a rose colored hydrate form.

The fusibility in the system KCl - $CoCl_2$ was studied by M. S. Golubeva and A. G. Bergman [7]. Two congruently fusible compounds were found, namely $CoCl_2 \cdot 2KCl$ and $5CoCl_2 \cdot 9KCl$, and one incongruent one, $CoCl_2 \cdot KCl$. Spectrophotometric measurements agree with these data, Figure 2a. The curve 1a relates to the alloy $CoCl_2 \cdot KCl$. It can be seen that it joins the lines of spectra of octahedral and tetrahedral complexes with a quantitative predominance of the octahedral ones.

According to thermal analysis and crystal – optical measurements [8] a compound of $2NaCl \cdot CoCl_2$ composition is formed in the system NaCl – $CoCl_2$ below the eutectic point. The absorption spectrum of alloy $NaCl \cdot CoCl_2$ indicates the formation of a tetrahedral complex (Figure 2b, curve 1). Two phases are visibly conspicuous in the

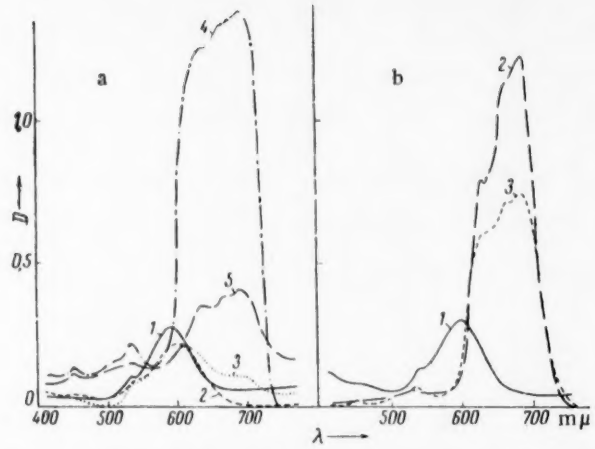

Fig. 1. Absorption spectrum of alloys in systems $CsCl-CoCl_2$ (a), $RbCl-CoCl_2$ (b). The figure denotes the following molar ratios of $MCl/CoCl_2$. a: 1) 0, 2) 0.9, 3) 1, 4) 2, 5) 326; b: 1) 1, 2) 2, 3) 47.

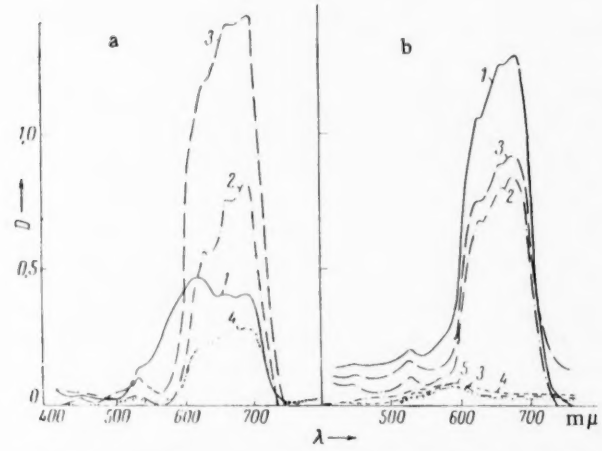

Fig. 2. Absorption spectrum of alloys in systems $KCl-CoCl_2$ (a), $NaCl-CoCl_2$ (b). The figures denote the following molar ratios of $MCl/CoCl_2$. a: 1) 1, 2) 1.8, 3) 2, 4) 900; b: 1) 1, 2) 2, 3) 4, 4) 5, 5) 105.

alloy $2NaCl \cdot CoCl_2$: the tetrahedral and the weakly absorbing octahedral. Curve 2 (Figure 2b) represents the absorption spectrum of the tetrahedral phase. Alloys with high NaCl contents continue preserving both phases mentioned. Here the portion of the octahedral phase grows. For alloys such as $4NaCl \cdot CoCl_2$ and $5NaCl \cdot CoCl_2$ we were able to separate these phases. The corresponding absorption spectra are illustrated by curves 3 and 4 (Figure 2b). The alloy with NaCl to $CoCl_2$ ratio of 105 contains only the octahedral dendrite phase, curve 5 (Figure 2b). Obviously it represents the self limited solid solution of $CoCl_2$ replacing NaCl. The character of the ionic coordination in Co^{2+} remains the same.

Alloys of $CoCl_2$ with LiCl are uniform throughout the whole range of component proportions not only in outward appearance, but also in optical properties. In bonds with similar ionic radii Co^{2+} (0.82) and Li^+ (0.78) their mutual continuous replacement in the crystal lattices of $CoCl_2$ and LiCl is possible while preserving the octahedral

cubic form for the Co^{2+} ion. Figure 3 shows that the absorption spectrum of alloys in the system $LiCl-CoCl_2$ retains the lines characteristic of the octahedral complexes in the wide range of component ratios. The optical data agree with results of fusibility studies in that same system [9], and they contradict the results of Ferrari and Baroni [10] (the fusibility curve has two minima and a maximum, which correspond to the compound Li_2CoCl_4).

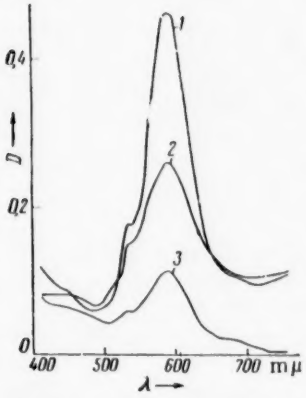

Fig. 3. Absorption spectrum of alloys in the system $LiCl-CoCl_2$. The figures denote the following molar ratios of $LiCl/CoCl_2$: 1) 0.085; 2) 2; 3) 200.

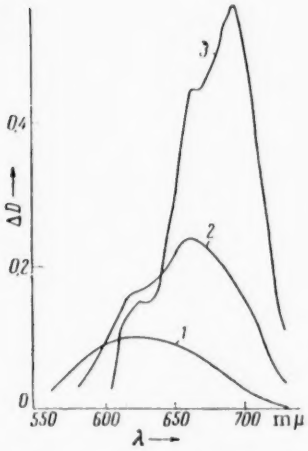

Fig. 4. Differential absorption curves of 0.00248 M solutions of $Co(NO_3)_2$ in a nitrate melt containing various quantities of KCl. Curves 1, 2 and 3 relate to the following pairs of molar concentrations of KCl, respectively: 0.139 and 0.000, 0.282 and 0.139, 1.635 and 0.282.

The cobalt ion in chloride complexes can exist in tetrahedrons or octahedrons, with preference for tetrahedrons. The tendency to enter octahedrons decreases from Cs to Li for complex compounds with the alkali metal atom in the outer sphere. At the same time the similar ionic radii of Co^{2+}, Na^+, and Li^+ create the condition for Co^{2+} to enter the lattice of NaCl and specially of LiCl, while retaining the octahedral coordination. The tendency to form higher complexes decreases from Cs to Li.

In the octahedral crystalline field the ^4F plane of the Co^{2+} ion cleaves to three equal planes G_4, G_5, and G_2. The next plane which does not cleave in the octahedral field, is ^4R. In accord with this the infrared region should show bands which represent the conversions $^4F(G_4) \rightarrow {}^4F(G_5)$ and $^4F(G_4) \rightarrow {}^4F(G_2)$ for small cleavage. The transition band $^4F(G_4) \rightarrow {}^4R(G_4)$ should be in the visible region for a weak crystalline field. Actually, the center of gravity of the main band in the visible region is at 590 and 600 mμ for compounds $CoCl_2$ and $MeCoCl_3$. Assuming for the transition F – R $\gamma = 3/5\,(E_1 - E_2) + 15400$ [11], where $E_1 - E_2$ is the cleavage of the F plane and 15400 cm^{-1} is the distance between F and R planes in the free ion Co^{2+}, we find $E_1 - E_2 = \sim 3300$ cm^{-1} for $CoCl_2$ and 2200 cm^{-1} for $MeCoCl_3$. If we do not take into account the shifting of the R plane in a crystal field, the introduction of an alkali metal into the outer sphere of a complex sharply lowers the strength of the crystal field, and consequently leads to a lowering of the already weak extra stabilizing force of the octahedral field over the tetrahedral one [12]. It is characteristic that the substitution of Na^+ and Li^+ ions by Co^{2+} ions in alkali chlorides is not connected with a shift in the octahedral band belonging to $CoCl_2$ even when in solid solutions with LiCl.

The preference of a cobalt ion for the tetrahedral sphere is reflected in the chemistry of its solutions. Differential curves of absorption spectra of two solutions of $Co(NO_3)_2$ in a nitrate melt, containing varying amounts of KCl, were constructed according to data in a previous paper [13]. In our opinion the picture thus obtained characterizes absorption bands of those complexes which are in the studied concentration range of substances added in large quantities. Curve 3 on Fig. 4 is analogous to those curves which we obtained from tetrahedral crystalline complexes. It can be seen that the absorption maxima of lower complexes belong to approximately 620 and 660 mμ. Earlier [13] we expressed the opinion that complex particles such as $[CoCl_2]$ and $[CoCl_3]^-$ correspond to those bands. When we take into account the fact that the absorption maximum of the higher nitrate complex pertains to 550 mμ [13], and the maximum of octahedral $[CoCl_3]^{4-}$ ion is around 590 mμ, then the complexes $[CoCl_2]$ and $[CoCl_3]^-$ should be ascribed the tetrahedral structure and the composition $[CoCl_2(NO_3)_2]^{2-}$ and $[CoCl_3NO_3]^{2-}$.

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ALKYLATION OF AROMATIC HYDROCARBONS

ALKYLATION OF NAPHTHALENE BY PROPYLENE ON AN ALUMINOSILICATE CATALYST AT MODERATE TEMPERATURES

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The alkylation of hydrocarbons by olefins with the help of various catalysts as a rule is accompanied by side reactions: isomerization, disproportionation, destruction, etc. The course of these reactions is determined by the nature of the catalyst used and the reaction conditions during alkylation. The side reactions can be suppressed by the choice of catalyst possessing a determined complex of properties, and by optimal alkylation conditions.

Such catalysts can be aluminosilicates when used for the alkylation of hydrocarbons, in particular aromatic ones, by olefins at tolerably low temperatures. The lower temperature limit of the alkylation is determined by the temperature conditions of polymerization suppression – a reaction which has the least activation energy of all the side reactions. The upper limit is determined by the maximum yield of monoalkylaromatic hydrocarbon desired.

The use of aluminosilicates during the alkylation of aromatic hydrocarbons has long been disputed [1]. The catalysts mentioned have been used successfully [2] for the alkylation of benzene and toluene by propylene, butylenes, and amylenes, at 450-480° and 140-160 atm. Benzene can be alkylated by ethylene in the presence of synthetic aluminosilicate at atmospheric pressure and 400° [3]. At 250° naphthalene is alkylated on diatomite by olefins with six or more carbon atoms [4]. Heating of ethylnaphthalene [5] with activated gumbrin clay at 230-240° and atmospheric pressure brings about a redistribution of the alkyl group; the reaction products are naphthalene, di- and triethylnaphthalenes. More extensive changes occur at 275°; ethylbenzene, ethane, tetrahydronaphthalene, and $(C_{10}H_7)_2$ are formed. The activation of gumbin with hydrogen chloride [6] allows one to lower the reaction temperature during the alkylation of aromatic hydrocarbons to 70°; even under those conditions side reactions take place: Isomerization of alkylaromatic hydrocarbons. We have shown [7] that the alkylation of aromatic hydrocarbons such as benzene and toluene, by propylene on a commercial aluminosilicate catalyst takes place, respectively, at + 20° and 0° at rapid rates. It is interesting to study alkylation of aromatic hydrocarbons on aluminosilicate catalysts at low temperatures from the viewpoint of being able to study a reaction with a minimum of complicating side processes.

In the work mentioned the reaction between naphthalene and propylene was used as an example to investigate further the low temperature alkylation on aluminosilicate catalysts.

It was found that the isopropylnaphthalene obtained on the aluminosilicate at 50° (in solution) and at 100°, in its isomeric structure was identical with the isopropylnaphthalene obtained by means of $H_3PO_4 \cdot BF_3$ [8] at 20° and 50°. The alkylation temperature of 100° for naphthalene on aluminosilicate catalysts seems to be the minimum for a reaction least complicated by side processes. In that case about 80% 1-isopropylnaphthalene and 20% 2-isopropylnaphthalene is formed. Increasing the alkylation temperature increases the alkylation rate of naphthalene, but at the same time considerable intramolecular isomerization of isopropylnaphthalene begins to take place. In addition, at 150° disproportionation of isopropylnaphthalenes formed occurs. At the expense of this reaction naphthalene is formed: at 100°, 1-2%, at 200°, about 4%, and at 250° about 9%.

Data on the isomeric composition of alkylates obtained at various temperatures with the help of aluminosilicate catalysts are given in Table 1.

An increase in the alkylation temperature increases the content of 2-isopropylnaphthalene in the alkylate. One can assume that during the alkylation of naphthalene the isopropyl group goes to the 1-position, and the formation of 2-isopropylnaphthalene must be explained by isomerization of 1-isopropylnaphthalene.

A comparison of isomeric compositions of isopropylnaphthalenes obtained at low temperatures in the presence of various catalysts shows, that in all cases they are identical (the alkylation was carried out under conditions where the side processes were reduced to a minimum).

We believe that the data obtained on isomerization of 1-isopropylnaphthalene of about 96% purity are sufficient proof of the assumptions. The isomeric composition of the reaction products was determined spectroscopically.

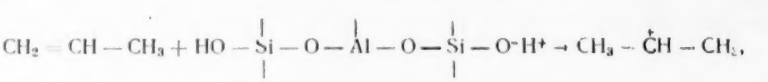
TABLE 1. Isomeric Composition of Isopropylnaphthalene Obtained at Various Alkylation Temperatures

Alkylation temperature in °C	Composition of isopropylene in %	
	1-isopropylnaphthalene	2-isopropylnaphthalene
100	80	20
100	79	21
150	63	37
200	56	44

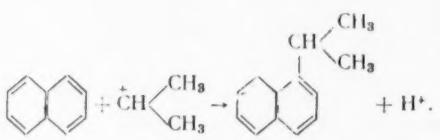
The isomerization was done in a reactor used for the alkylation of naphthalene. The conditions for the isomerization of isopropylnaphthalene (time of contact, temperature, etc.) were so selected that they corresponded exactly to the conditions of naphthalene alkylation on an aluminosilicate catalyst. The change in the isomeric composition of isopropylnaphthalene with isomerization temperature is given in Table 2. The experiments were first done with 1-isopropylnaphthalene, and later with a mixture of isopropylnaphthalenes obtained from the alkylation of naphthalene at 100°. In both the first and second case identical results were obtained.

A comparison of the compositions of isopropylnaphthalenes obtained by alkylation (Table 1) and isomerization (Table 2) makes one think that in the former case the addition of the alkyl group takes place at position 1, and that 2-isopropylnaphthalene is formed by intramolecular migration of the alkyl group to the adjacent position 2.

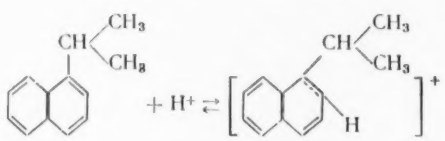
The formation of isomers in reactions conducted with the help of aluminosilicate catalysts can be explained quite well when we consider the structure of aluminosilicates in the light of a carbonium mechanism. On the surface of the catalyst a molecule of propylene forms the carbonium ion



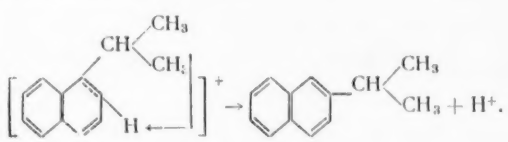
which then reacts with a naphthalene molecule, giving 1-isopropylnaphthalene



Then 1-isopropylnaphthalene forms a complex on the catalyst surface, adding a proton



Then the alkyl group migrates to the adjacent position 2.



The proton adds to the aluminum complex of the catalyst. Thus the 1-isopropylnaphthalene is formed by alkylation of naphthalene on an aluminosilicate catalyst by propylene, and the 2-isomer is obtained on isomerization of 1-isopropylnaphthalene on the aluminosilicate catalyst.

EXPERIMENTAL

The experiments were conducted on a periodically running laboratory setup [7]. The catalyst was commercial aluminosilicate catalyst: granular, weight 0.634 g/cm^3, unit surface 490 m^2/g, specific volume 0.44 cm^3/g, activity index 34 [9]. Freshly filled catalyst was activated by air (1000 ml air per 1 ml catalyst per hour) at 380° over a period of three hours. Adsorbed alkylate was removed from the catalyst (0.347 g with 1 g catalyst), then the catalyst was regenerated by blowing air through it at 400° and 30 minutes, then steaming for five minutes (0.8 ml water per 1 ml catalyst), again treated with air, and so on till no more CO_2 was present in the waste gases. After regeneration the catalyst had practically the same activity index as in the beginning.

We used 350 ml catalyst per experiment; the ratio of the catalyst bed height to the internal diameter of the reactor cross section (wall thickness 1.5 mm) was 14, which ensured satisfactory conversion of propylene (84% at a feeding rate of propylene of 12 liter/hour).

TABLE 2. Composition of Isopropylnaphthalene after Isomerization on Aluminosilicate Catalyst at Various Temperatures

Composition of initial isopropylnaphthalene	Isomerization temperature in °C	Composition of isopropylnaphthalene after isomerization
1-Isopropylnaphthalene 96%	100	1-Isopropylnaphthalene 80% 2-Isopropylnaphthalene 20%
1-Isopropylnaphthalene 79% 2-Isopropylnaphthalene 21%	150	1-Isopropylnaphthalene 64% 2-Isopropylnaphthalene 36%
1-Isopropylnaphthalene 80% 2-Isopropylnaphthalene 20%	200	1-Isopropylnaphthalene 54% 2-Isopropylnaphthalene 46%

TABLE 3. Composition of Alkylates (weight %) Obtained at Various Molar Ratios of Naphthalene Propylene (reaction temperature 100°)

Naphthalenes	1:2		1:1		2:1	
	crude alkyl	alkylate	crude alkyl	alkylate	crude alkyl	alkylate
Naphthalene	21.4	–	28.8	–	50.5	–
Isopropylnaphthalene	22.9	29.2	29.4	41.3	37.4	75.6
Diisopropylnaphthalene	27.2	34.6	23.9	33.5	9.3	18.8
Triisopropylnaphthalene	20.0	25.4	11.5	16.2	2.0	4.0
Tetraisopropylnaphthalene	8.5	10.8	6.4	9.0	0.8	1.6
	Theoretical yield					
Isopropylnaphthalene	29%	–	42%	–	66%	–

TABLE 4. Composition of Alkylates (weight %) Obtained at Various Reaction Temperatures (molar ratio naphthalene/propylene = 1/1)

Naphthalenes	Alkylate composition			
	50°	100°	150°	200°
Naphthalene	30.0	29.0	28.0	24.0
Monoisopropylnaphthalene	30.0	30.0	37.0	44.0
Diisopropylnaphthalene	23.6	24.0	23.0	18.0
Triisopropylnaphthalene	10.8	11.0	2.0	6.0
Tetraisopropylnaphthalene	5.6	6.0	5.0	8.0
	Theoretical yield			
Isopropylnaphthalene	43%	42%	52%	58%

As raw material we used Naphthalene Tu MKhP 1571-47 and 99% pure propylene. The effect of various factors on the yield and composition of reaction products was studied: effect of molar ratios of reacting components (naphthalene/propylene) at 100° (Table 3), and experiment temperature (Table 4). The feeding rate of propylene was maintained at 12 liters/hr in all cases. The composition of the alkylate was determined by triple distillation in a vacuum column with 24 theor. plates efficiency, and spectroscopically; it was determined that the alkylate consists, depending on conditions, of mono-, di-, tri-, and tetraisopropylnaphthalenes. The physicochemical properties of synthesized alkylnaphthalenes are given in Table 5.

TABLE 5. Properties of Isopropylnaphthalenes Synthesized on an Aluminosilicate Catalyst

Alkylnaphthalene	Boiling point in °C	Melting point in °C	$n^{20}D$	d^{20}_4	Mol. wt.
1-Isopropylnaphthalene	264-266	–	1.5751	0.9009	171
2-Isopropylnaphthalene	267-260	–	1.5770	0.9798	172
Isopropylnaphthalene	264-270	–			170
Diisopropylnaphthalene	165-170/2	–	1.5700	0.9636	215
Triisopropylnaphthalene	190-195/2	–	1.5620	0.9610	253
Tetraisopropylnaphthalene	–	128-129	–	–	296

We studied the alkylation of naphthalene by propylene at atmospheric pressure and various temperatures on an aluminosilicate catalyst, and found, that the alkylation of naphthalene goes to position 1. During the reaction occurs intramolecular migration of the alkyl group and the result is a mixture of isomeric products.

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IMINATION OF 2-SUBSTITUTED INDANDIONES-1,3

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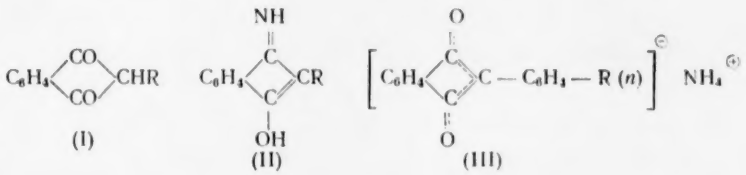
In previous papers we demonstrated that 2-phenyl- [1] and 2-methylindandione-1,3 [2] (Ia and b) with ammonium acetate in glacial acetic acid give the imino structures II (a,b). Furthermore, we tried to clarify whether the reaction described above was universal for 2-aryl- and 2-alkylindandiones-1,3.



(I) (II) (III)

In I or II R: a = C_6H_5; b = CH_3; c = C_2H_5; d = $CH(C_6H_5)_2$; e = 9-xanthyl; f = p-$CH_3OC_6H_4$; g = p-NO_2-C_6H_4; h = α-$C_{10}H_7$.

Six new imino derivatives of 2-substituted indandiones (IIc-h) were synthesized. Imines of 2-alkylindandiones (IIb-d) are more soluble in organic solvents than are their analogs with a phenyl group in the 2-position (IIa, f-g) (see [1,2]). Imines (IIb, c) are slightly soluble in boiling water. The imine of 2-xanthylindandione (IIe) has properties similar to those of imines of 2-arylindandiones; compounds (IIa, e-g) have relatively higher melting points and are difficultly soluble in weakly polar solvents. Imines of 2-α-naphthylindandione (IIh) in their physical properties are between the two imine groups mentioned.

All imines, when boiled in alcohol acidified with hydrochloric acid, and hydrolyzed to the corresponding 2-substituted indandiones. Only in the case of the imine of 2-xanthylindandione partial dexanthylation of the diketone takes place in addition to the hydrolysis.

It was interesting, from a theoretical viewpoint, to see the imination of 2-p-nitrophenylindandione (Ig), which compound is somewhat different, in its acidity and other properties, from the rest of 2-arylindandiones [3]. This compound on imination at first forms only the ammonium salt of 2-nitrophenylindandione (III, R = NO_2), which is stable in an acetic acid medium with a sufficient excess of ammonium acetate. But at elevated temperatures (ammonium propionate in propionic acid) the desired imine is slowly formed (II g). The ammonium salt of 2-phenylindandione (III, R = H) synthesized in another way, does not precipitate in an acetic acid medium in the presence of excess ammonium acetate; the solution thus obtained on boiling gives the imine of phenylindandione. In this connection it is assumed, that the imination of 2-p-nitrophenylindandione proceeds to the extent that the salt (III, R = NO_2) succeeds in thermally dissociating to the initial β-diketone and ammonia. Then occurs a nucleophilic attack on the 2-p-nitrophenylindandione molecule by an ammonia molecule with the formation of the corresponding imine. Incidentally, formation of the ammonium salt of the β-ketone as a side product during synthesis of β-aminovinylketones was mentioned before [4].

The imine of 2-p-nitrophenylindandione (IIg) has weakly acidic properties. It is slightly soluble in aqueous alkalies on heating and gives a bright red coloring (addition of some alcohol to the mixture improves the solubility).

Table 1 gives some information on recently synthesized compounds.

EXPERIMENTAL*

Ethylindandione imine (IIc). Two g ethylindandione (Ic) [5] was heated to boiling in 6 ml glacial CH_3COOH and 6 g ammonium acetate. The mixture was cooled and to it was added gradually 24 ml water, with a stirring rod,

*Some physical properties and yields are given in Table 1.

Imines of 2-Substituted Indandiones-1,3

Compound	M. p. in °C	Color	Solvent for crystallization	Yield in %
II c	168-169	Red	CH_3OH; CH_3OH + + H_2O (1:1)	68
II d	205.5-206.5	Orange-red	C_2H_5OH	65
II e	265-266	Orange-yellow	Butylcellosolve	
			CH_3COOH	96
II f	260-265	Red	CH_3COOH	88
II g	289	Brick red	CH_3COOH	90
II h	202.5-203.5	Brick red	$C_6H_5CH_3$	Insig-nificant
III R = NO_2	258-260	Dark brown	–	75
III R = H	–	Dark brown	–	93

covering the flask walls. The next day the imine was separated (IIc), 1.37 g; it dissolved in the usual organic solvents, difficultly in boiling water.

Found %: N 8.31. $C_{11}H_{11}ON$. Calculated %: N 8.09.

Benzhydrylindandione imine (IId). Benzhydrylindandione (1 g) (Id) [6] was boiled in 10 ml glacial CH_3COOH with 6 g ammonium acetate for half an hour. To this was added 1 ml water and the mixture was cooled, while the flask walls were covered by means of a stirring rod. The next day the imine (IId), 0.65 g, was separated; it dissolved moderately in alcohols and other polar solvents.

Found %: N 4.58. $C_{22}H_{17}ON$. Calculated %: N 4.50.

Xanthylindandione imine (IIe). Xanthylindandione (0.5 g) (Ie) [7] in 5 ml glacial CH_3COOH was digested with 3 g ammonium acetate for a few minutes. The mixture was cooled and the imine separated (IIe), 0.48 g. The substance hardly dissolved in low boiling solvents, except for acetic acid; it dissolved more readily in decalin, glycol ethers or diethyleneglycol.

Found %: N 4.27. $C_{22}H_{15}O_2N$. Calculated %: N 4.31.

α-Naphthylindandione imine (IIh). One g α-naphthylindandione (Ih) [8] was digested in 5 ml glacial CH_3COOH with 10 g ammonium acetate for 10 minutes. A red tar was formed on cooling. It was dissolved in alcohol, and poured into water. The imine (IIh) was filtered. The compound dissolved more readily than did the imines of 2-arylindandiones, in nonpolar and slightly polar solvents.

Found %: N 5.27. $C_{19}H_{13}ON$. Calculated %: N 5.16.

p-Methoxyphenylindandione imine (IIf). 1.5 g p-methoxyphenylindandione (If) [9] was digested for 10 minutes in 20 ml glacial CH_3COOH with 4.5 g ammonium acetate. The mixture was cooled and the imine (IIf) separated, 1.33 g; it was sparingly soluble in alcohols, somewhat more readily in acetic acid.

Found %: N 5.38. $C_{16}H_{13}O_2N$. Calculated %: N 5.58.

Ammonium salt of 2-phenylindandione (III, R = H). Dry ammonia was passed for one hour over a heated solution (to 100-110°) of 3 g phenylindandione in 30 ml xylol. The mixture was cooled under a slight stream of ammonia, and the salt (III, R = H) 3 g, filtered. The salt was readily soluble in water and alcohols, but insoluble in hydrocarbons and weakly polar solvents. The dry salt on heating in air decomposed to phenylindandione and ammonia, and when the salt was heated in a sealed tube (or its solution in ethylene glycol at 150-170°), the imine of phenylindandione (IIa) was formed. With acetic acid phenylindandione and ammonium acetate were formed first; on heating of that solution the imine (IIa) was obtained.

Found %: N 5.91. $C_{15}H_{13}O_2N$. Calculated %: N 5.85.

Ammonium salt of p-nitrophenylindandione (III, R = NO_2). 0.5 g p-nitrophenylindandione (Ig) [10] was dissolved in 20 ml glacial CH_3COOH under boiling, and to it was gradually added about 1.5 g ammonium acetate.

After a few minutes all crystallized to a thick, matted mass. The yield of the salt (III, R = NO_2) was 0.4 g. The salt dissolved readily in water and alcohols. Boiling acetic acid decomposed the salt to p-nitrophenylindandione; a boiling solution with excess ammonium acetate reprecipitated the ammonium salt of the diketone. Mineral acids completely decompose the salt.

Found %: N 9.68. $C_{15}H_{12}O_4N_2$. Calculated %: N 9.86.

p-Nitrophenylindandione imine (II g). 0.5 g p-nitrophenylindandione (Ig) was digested in 3 ml propionic acid for 27 hr with 3 ml ammonium propionate. The dark brown ammonium salt of the initial diketone gradually dissolved. The solution was cooled, the imine (IIg) filtered, 0.45 g. The substance hardly dissolved in hydrocarbons, ether, and other weakly polar solvents; better in alcohols and acetic acid, readily in dimethylformamide.

Found %: N 10.27. $C_{15}H_{10}O_3N_2$. Calculated %: N 10.52.

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ALKYLATION OF TETRAHYDROFURAN BY ETHYLENE

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The attention of many an investigator today has been drawn to the problem of alkylation of alkanes. Since it has been established that paraffinic hydrocarbons can be alkylated, it is natural to expect that an analogous reaction could occur with saturated cyclic compounds. The alkylation of cyclanes has been little studied. The alkylation of saturated oxygeneous cyclic compounds generally has not been studied. An approximate calculation on our part showed that such a reaction is thermodynamically possible.

In this paper we first show the possibility of alkylating tetrahydrofuran by ethylene at elevated temperatures and pressure. We also studied the effect of temperature, duration of experiment, and component ratios, on the reaction course and the yield of α-ethyltetrahydrofuran.

EXPERIMENTAL

The alkylation was done in a rotating autoclave of 250 ml capacity. It was charged with 0.75 gram mole of tetrahydrofuran, then the air was displaced with ethylene, the required pressure established, and the heat connected. After completion of the experiment the autoclave was cooled, the residual pressure released, and the catalyzate formed dried over potash. The catalyzate was distilled from a Favorskii flask in three fractions:(I) to 64°;(II) 64-70°; (III) 70-120°, and the residue boiling above 120°. The separated fractions were analyzed by gas liquid chromatography [1] on a 2-meter column filled with diatomite impregnated with tricresyl phosphate. Hydrogen passing through a column at 40 ml/hour was used as gas carrier. At the same time the structure of alkyltetrahydrofurans according to the number of CH_2- and CH_3- groups was determined by infrared spectroscopy [2]. Spectra of narrow fractions were taken on a UR-10 apparatus in CCl_4 solution on a LiF prism in the region 2800-3100 cm^{-1}, concentration 0.1-0.03 gram-mole/liter. Thickness of the absorbing layer was 0.25 mm. Cuvet of constant dimension of 1 ml. The intensities of bands corresponding to asymmetric valence vibrations of the CH_2- and CH_3-groups were measured.

We also determined the elementary composition of alkyltetrahydrofurans.

An autoclave was charged with 2 gram mole tetrahydrofuran and the alkylation was conducted at 325° with initial pressure of ethylene at 25 atm, over a period of 1 hr; after incorporation of the ethylene the autoclave was heated for another hour at the same temperature. Distillation of the catalyzate on an efficient column gave an individual compound boiling at 105-106° at 751 mm Hg, $n^{20}D$ 1.4151, and d^{20}_4 0.8542.

Measurement of band intensities for 2937 and 2967 cm^{-1} showed that the compound has only one CH_3- and four CH_2-groups, which corresponds to the structure of ethyltetrahydrofuran.*

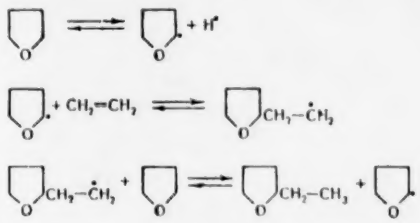
The elementary composition of the compound obtained agrees with the one calculated theoretically for ethyltetrahydrofuran.

Found %: C 72.30, 72.34; H 12.17, 12.23. $C_6H_{12}O$. Calculated %: C 71.94; H 12.08.

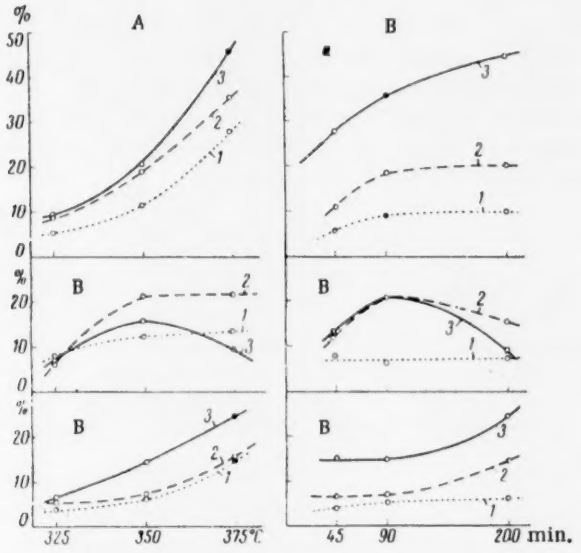
Literature data for α-ethyltetrahydrofuran: boiling point 105-106°, $n^{20}D$ 1.4165; d^{20}_4 0.8563 [3], and for β-ethyltetrahydrofuran: boiling point 115.5-116.5°, $n^{20}D$ 1.4204; d^{20}_4 0.8601 [4] indicate that under the conditions described above, the alkylation of tetrahydrofuran goes to the α-position. In chromatographic analysis the peaks of the ethyltetrahydrofuran obtained and of standard α-ethyltetrahydrofuran coincided.

*We thank B. V. Lopatin for the spectra.

The thermal alkylation of tetrahydrofuran obviously takes place by a mechanism which is analogous to that of thermal alkane alkylation [5]:



In this paper we bring the results of studying the effect of temperature, duration of experiment, and ratio of components, on the degree of conversion of tetrahydrofuran, the yields of α-ethyltetrahydrofuran, and of polyalkylate.* For this purpose a series of three experiments was devised for alkylation of tetrahydrofuran over a period of 45, 90, and 200 minutes. Preliminary experiments established, that below 300° the alkylation hardly takes place, and above 400° side reactions develop rapidly. For this reason each series of experiments was conducted at 325, 350, and 375°.



Effect of temperature (A) and duration of experiment (B) on the conversion degree of tetrahydrofuran (a), and on the yield of α-ethyltetrahydrofuran (b) and polyalkylate (c). For A: 1) duration of experiment 45 min; 2) 90 min; 3) 200 min. For B: 1) temp. 325°; 2) 350°; 3) 375°.

On figure A are represented curves obtained when the dependency of the conversion degree of tetrahydrofuran and the yields of α-ethyltetrahydrofuran and polyalkylate on the temperature were studied. Figure B shows the curves obtained on studies of the effect of duration of experiment on the conversion degree of tetrahydrofuran, and the yield of α-ethyltetrahydrofuran and polyalkylate.

Analysis of the figure indicates, that the optimum conditions for the alkylation of tetrahydrofuran are a temperature of 350° and 90 minutes duration. At higher temperatures the conversion degree increases rapidly as a result of considerable formation of low-boiling products at the expense of side reactions.

* By polyalkylate we conditionally mean the residue which boils higher than does α-ethyltetrahydrofuran.

Effect of the Ratio Tetrahydrofuran/Ethylene on the Composition of the Catalyzate

Expt. No.	Ethylene pressure, atm	Conversion degree of tetrahydrofuran			Yield of α-ethyltetrahydrofuran				Yield of polyalkylate		Weight of catalyzate
		grams	% per charge	% per catalyzate	grams	% per initial	% per reacted	% per catalyzate	grams	% per catalyzate	
1	50	10.4	19.2	19	3	4	20.8	5.5	7.1	13	54.6
2	10*	3.9	7.2	7.4	0.6	0.8	11.1	1.1	1.7	3.4	52.4

* Plus 40 atm nitrogen.

Studies on the effect of tetrahydrofuran/ethylene component ratio on the conversion degree of tetrahydrofuran, and the yields of α-ethyltetrahydrofuran and of polyalkylate were conducted with 0.75 gram mole tetrahydrofuran at 350° and a duration of 90 minutes. The table shows, that an increase in the pressure of ethylene leads to a considerable increase in the yields of α-ethyltetrahydrofuran and also of products of much more extensive alkylation.

The results of our work show the possibility of thermal alkylation of saturated oxygeneous cyclic compounds.

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SYNTHESIS OF β-CEDRENE

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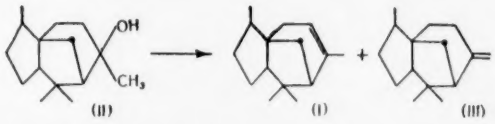
Natural cedrene has a lower angle of rotation than α-cedrene (I), which is prepared by dehydration of cedrol (II). Naves, Papazian and Perrottet [1] showed that this difference may be explained by nonhomogeniety of the natural product.

Identification of the products of the oxidative cleavage of substituted cyclopropanecarboxylic acids, which were synthesized by these authors by condensation of natural cedrene with ethyl diazoacetate, led them to the conclusion that the natural hydrocarbon contains β-cedrene III – a compound with an esocyclic double bond – as an impurity.

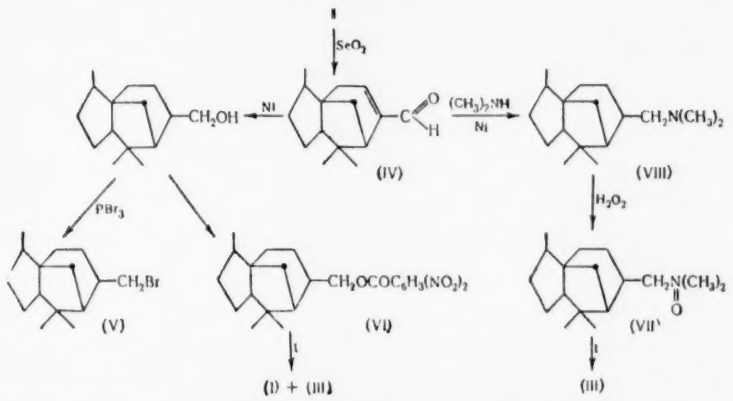
The formation of natural cedrene must take place in accordance with the following scheme:



However, β-cedrene has not been obtained as an individual compound up to the present time. The synthesis of β-cedrene is described in the present article.

The course of the synthesis was based on the oxidation of cedrene to cedrenal IV with selenium dioxide, as described by Treibs [2], and it may be represented by Scheme I.

Scheme I



The preparation of β-cedrene by dehydrobromination of primary cedranyl bromide was not possible, since the latter remained unchanged under the influence of alcoholic alkali, boiling ethylpyridine, and sodium ethylate. Pyrolysis of primary cedranol 3,5-dinitrobenzoate (VI) led to a mixture of α- and β-cedrenes. In addition to frequencies at 1625, 3075, and 887 cm^{-1}, which are assigned to the $R_2C = CH_2$ group, the i.r., spectrum of the pyrolysis product contained frequencies at 1660 and 3022 cm^{-1}, which are characteristic of the secondary-tertiary double bond of α-cedrene. The vigorous reaction conditions (280-350°) apparently cause isomerization of β-cedrene to α-cedrene.

It may be remarked that the conversion of β-pinene to α-pinene proceeds so smoothly that the reaction was used by Rudakov [3] for the preparation of α-pinene of the highest optical purity.

We were able to prepare very pure samples of β-cedrene by pyrolysis of dimethyl-prim-cedranylamine N-oxide (VII).

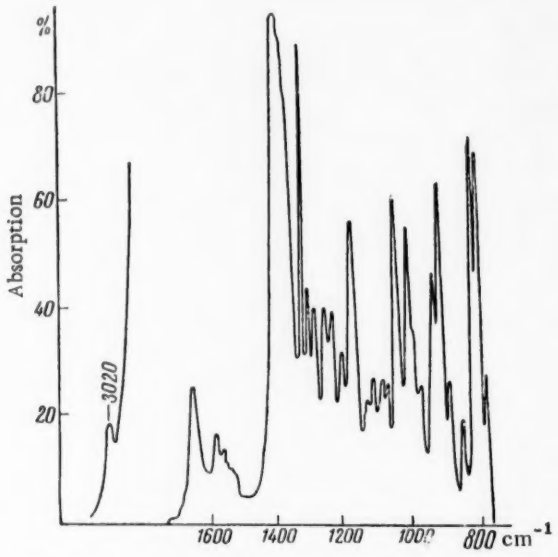


Fig. 1. I. r., spectrum of α-cedrene prepared by dehydration of cedrol. NaCl and LiF prisms; l = 4μ; IKS-14.

According to Cope [4], cleavage of N-oxides of tertiary amines is the mildest pyrolytic method for the preparation of olefins. The β-cedrene prepared by the above method was a colorless liquid with the following constants: $n^{20}D$ 1.5047; d^{20}_4 0.9350; $[\alpha]^{20}D$ + 11.3° (heptane, C = 13.6).

In the infrared spectrum of β-cedrene there were intense bands at about 1625 and 887 cm^{-1} and a band with a frequency of 3075 cm^{-1}, which is characteristic of the double bond attached to an esocyclic methylene group. Hydrogenation over platinum gave cedrane, the properties of which were very close to those of cedrane from α-cedrene.

EXPERIMENTAL

The α-cedrene was prepared by dehydration of cedrol separated from the ester oil of Cossack juniper (Juniperus sabina L.); it had the following constants: $n^{20}D$ 1.4982; d^{20}_4 0.9343; $[\alpha]^{20}D$ − 93.5°.

The cedrenal was prepared by the method of Treibs [2], somewhat modified, and was obtained in a yield of 72-75% as against 50-55% obtained by Treibs; $n^{20}D$ 1.5195; d^{20}_4 1.0202; $[\alpha]^{20}D$ − 65.5°.

The primary cedranol was obtained in quantitative yield by hydrogenation of cedrenal over skeletal nickel at 70 atm and 60°. It was a colorless, viscous liquid; b. p. 143-144°/1 mm; $n^{20}D$ 1.5095; d^{20}_4 1.0110; $[\alpha]^{20}D$ − 17.0°; MR found 65.68; calculated 66.29.

Found %: C 80.66; H 11.80. $C_{15}H_{26}O$. Calculated %: C 81.08; H 11.71.

The 3,5-dinitrobenzoate was prepared by the usual method; m. p. 80.5-81.5° (from petroleum ether).

Found %: N 6.92. Calculated %: N 6.72.

Pyrolysis of prim-cedranol 3,5-dinitrobenzoate (VI). A total of 7.5 g of (VI) was heated in a heat-resistant flask at 15 mm and 280-350°. The distillate was chromatographed on basic aluminum oxide (I-II activity). Petroleum ether eluted 1.30 g (35%) of hydrocarbon: $n^{20}D$ 1.5055; d^{20}_4 0.9317; $[\alpha]^{20}D$ − 34.6°; MR found 65.01; calculated 64.40.

Found %: C 88.23; H 11.52. $C_{15}H_{24}$. Calculated %: C 88.17; H 11.83.

Dimethyl-prim-cedranylamine VIII. This compound was prepared by hydrogenation of 22.2 g of IV over skeletal nickel catalyst obtained from 15 g of Ni/Al alloy; the reaction was carried out in 150 ml of a 4% solution of dimethylamine in ethanol at 120 atm and 80° with a reaction time of 4 hr. There was obtained 8.0 g (32%) of (VIII); b. p. 150-152°/1 mm; $n^{20}D$ 1.5033; d^{20}_4 0.9555; MR found 77.21, calculated 78.05. Hydrochloride m. p. 255.5-256° (from acetone).

Found %: N 4.66. $C_{17}H_{32}NCl$. Calculated %: N 4.83.

In addition, primary cedranol was obtained in 60% yield.

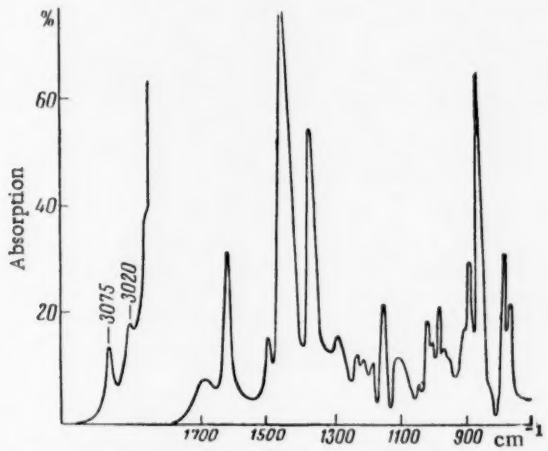


Fig. 2. I.r., spectrum of the product of pyrolytic decomposition of prim-cedranol 3,5-dinitrobenzoate. NaCl and LiF prisms, l = 4μ; IKS-14.

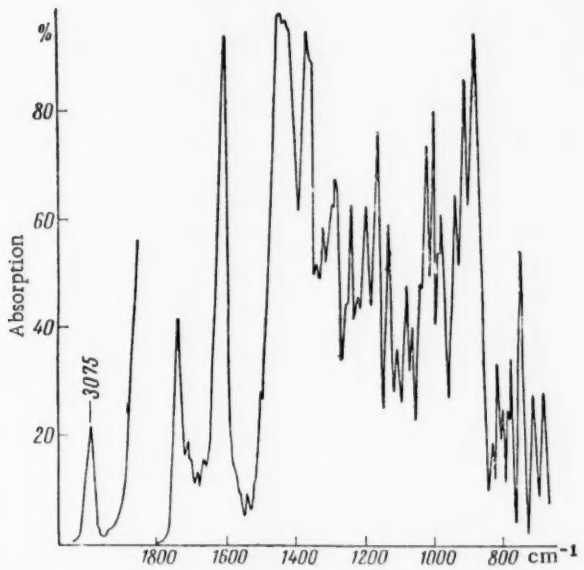


Fig. 3. I.r., spectrum of β-cedrene prepared from dimethyl-prim-cedranylamine N-oxide. NaCl and LiF prisms, l = 5μ; IKS-14.

Preparation of β-cedrene by pyrolysis of (VII). A mixture of 5.8 g of the amine, 10 ml of acetone, and 7 ml of 28% H_2O_2 was stirred at room temperature until solution of the product was complete. After decomposition of the excess hydrogen peroxide with platinum black and removal of the solvent under vacuum the product was pyrolyzed at 150-190°/1 mm. The distillate was washed free of unreacted dimethyl-prim-cedranylamine with hydrochloric acid and chromatographed on Al_2O_3 (I-II activity). There was obtained 1.50 g (31%) of β-cedrene as a colorless liquid with the following constants: $n^{20}D$ 1.5047; d^{20}_4 0.9350; $[\alpha]^{20}D$ +11.3 (heptane, C = 13.6); MR found 64.76; calculated 64.40.

Found %: C 88.08; H 11.72. $C_{15}H_{24}$. Calculated %: C 88.17; H 11.83.

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A NEW ROUTE FOR THE SYNTHESIS OF QUINOLIZIDINE DERIVATIVES

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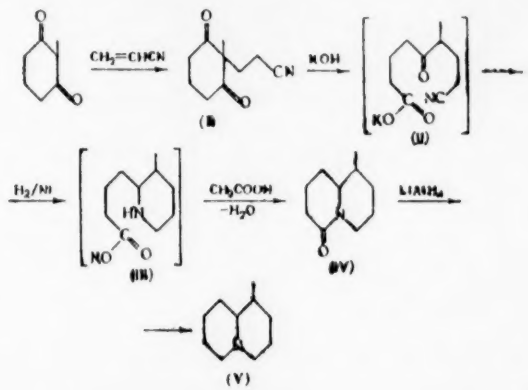
Quinolizidine (norlupinane) derivatives constitute an important group of heterocyclic compounds to which belong the alkaloids lipinine, lupanine, sparteine, anagyrine, and others [1]. Some of these possess clearly expressed physiological action and are used in medicine, for example, as respiratory stimulants [2, 3].

Construction of the quinolizidine system is accomplished by means of intramolecular alkylation and acylation of piperidine derivatives, which are usually prepared from the corresponding pyridine compounds [4].

In our current work, we have developed a new and simple route for the synthesis of quinolizidine derivatives from dihydroresorcinol in accordance with the following scheme:



Hydrogenation of 2-methyl-2-(β-cyanoethyl)dihydroresorcinol (I) over skeletal nickel in the presence of a base and subsequent treatment of the reaction product with acetic acid resulted in a high yield of 1-methyl-6-ketoquinolizidine (IV), the structure of which was confirmed by i.r., spectroscopy* (presence of a band characteristic of a lactam carbonyl, 1643 cm^{-1}) [5]. The reaction evidently proceeds through the intermediate stages of hydrolytic cleavage (I → II), reductive cyclization (II → III), and intramolecular acylation (III → IV). Reduction of the 1-methyl-6-ketoquinolizidine (IV) with $LiAlH_4$ led to the alpha form of D,L-lupinane (V), which was characterized as the picrate with an m. p. of 183-184°, sparingly soluble in methanol, and as the methiodide with an m. p. of 263-264°. The i.r., spectrum of this D,L-lupinane had frequencies (2802 and 2759 cm^{-1}) belonging to trans-quinolizidine compounds [6].

EXPERIMENTAL

The 2-methyl-2-(β-cyanoethyl)dihydroresorcinol (I) (b. p. 134-137° at 0.5 mm; $n^{20}D$ 1.4886) was prepared by the method developed by I. N. Nazarov and co-workers [7].

1-Methyl-6-ketoquinolizidine (IV). A solution of 16.9 g (0.094 mole) of 2-methyl-2-(β-cyanoethyl)dihydroresorcinol (I) in 100 ml of methanol was hydrogenated in the presence of 5.26 g (0.094 mole) of sodium hydroxide and about 1 g of skeletal nickel until three equivalents of hydrogen had been absorbed (80-85°, 85-70 atm, 12 hr). After separation of the catalyst and distillation of the methanol, the reaction product was refluxed for 1.5 hr with

*The i.r., spectra ($CHCl_3$) were taken by G. A. Kogan, for which the authors acknowledge their appreciation.

50 ml of acetic acid. The resulting solution was evaporated to dryness (~15 mm, 30-40°), the residue was treated with water, and 12.2 g (78%) of 1-methyl-6-ketoquinolizidine (IV), b. p. 99-103° at 0.8 mm and $n^{20}D$ 1.5095 was extracted with ether. Chromatography on II-activity aluminum oxide (elution with a 4:1 mixture of petroleum ether and benzene, with benzene, and with a 7:1 mixture of benzene and methanol) separated 8.8 g (55%) of 1-methyl-6-ketoquinolizidine with a b. p. of 88° at 0.5 mm, $n^{20}D$ 1.5085. Rf = 0.49 (chromatographic plate prepared with II-activity Al_2O_3; 1:1 mixture of benzene and acetone).

Found %: C 71.27, 71.45; H 10.20, 10.10; N 8.51, 8.34. $C_{10}H_{17}ON$. Calculated %: C 71.80; H 10.10; N 8.38.

D,L-Lupinane (V). To 1.7 g (0.04 mole) of $LiAlH_4$ in 250 ml of absolute ether was added 4.2 g (0.025 mole) of 1-methyl-6-ketoquinolizidine (IV) in 250 ml of absolute ether. The solution was refluxed with stirring for 5 hr, and was then treated at 0-3° with 10 ml of ethyl acetate. The mixture was stirred at 20° for 15 minutes, and was then extracted with 7 g of NaOH in 170 ml of water. From the ether layer was separated 3.2 g (84%) of D,L-lupinane (V) with a b. p. of 64-65° at 7 mm, $n^{20}D$ 1.4815. Rf = 0.7 (chromatographic plate prepared with II-activity Al_2O_3; 1:1 mixture of benzene and acetone).

Found %: C 78.52, 78.73; H 12.40, 12.41; N 9.13, 9.01. $C_{10}H_{19}N$. Calculated %: C 78.36; H 12.50; N 9.14.

The picrate (57% yield) had an m. p. of 183-184° (from methanol).

Found %: C 50.46, 50.44; H 5.73, 5.66; N 15.11, 14.91. $C_{10}H_{19}N \cdot (NO_2)_3C_6H_2OH$. Calculated %: C 50.26; H 5.80; N 14.65.

The methiodide had an m. p. of 263-264°.

Found %: N 4.59, 4.69. $C_{10}H_{19}N \cdot CH_3I$. Calculated %: N 4.75.

The literature reports the following properties for D,L-lupinane: b. p. 75-77°/11 mm; picrate, α-form, m. p. 187° [8], 185° [9], 192-193° [10, 11]; picrate, β-form, m. p. 163° [8, 12].

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o-[2,3(CO),6,5(CO)]-DIBENZOYLENISONICOTINOYL)BENZOIC ACID

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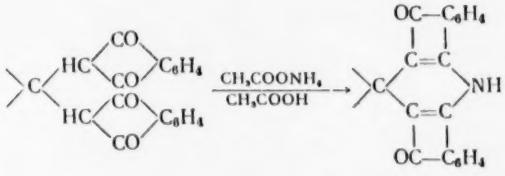
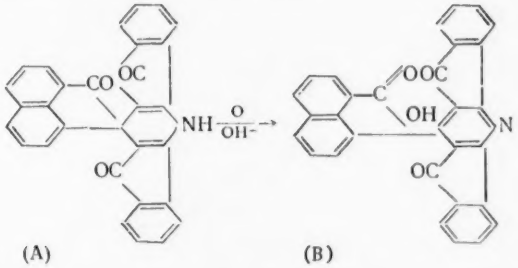
We have shown in previous work [1, 2] that gem diindanedionyl derivatives readily form the corresponding dihydropyridines under the action of ammonium acetate in glacial acetic acid:



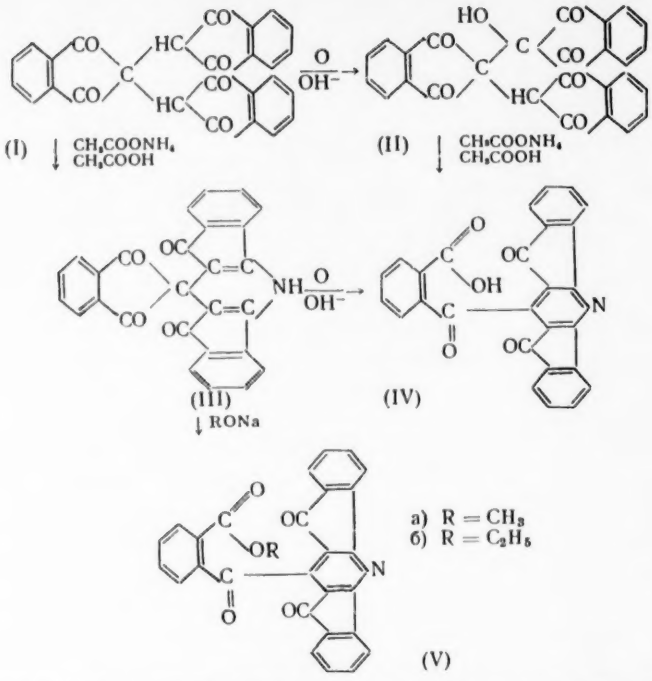
It was of interest to use in this reaction the product of the oxidation of trisindanedione (I) – hydroxytrisindanedione (II) [3, 4] – which should yield a derivative of 3-hydroxy-3,4-dihydropyridine. Reaction of the enol form of hydroxytrisindanedione with ammonium acetate in glacial acetic acid proceeds readily and rapidly with the formation of a yellow crystalline substance which is practically insoluble in bases at ordinary temperatures. A little dissolves in dilute bases and in sodium bicarbonate solution upon heating; the addition of a more concentrated solution of base causes precipitation of the salt. A number of pure salts were prepared. They were all sparingly soluble in water.

The same salts can also be prepared by oxidation of indanedione-1,3-spiro-(2:4')-2';3'(CO),6';5'(CO)-dibenzoylenedihydropyridine (III) with perhydrol in the presence of a base in an alcoholic medium. When these solutions are acidified, the same substance separates as is formed by the action of ammonium acetate on hydroxytrisindanedione. The ability of III to undergo oxidation in an alkaline medium to salt-like substances is reminiscent of acenaphthenone-1-spiro-(2:4')-2',3'(CO),6',5'(CO)-dibenzoylenedihydropyridine (A), which we studied earlier [2]. This compound undergoes oxidation in an alkaline medium to 8-(2',3'(CO),6',5'(CO)-dibenzoylenepyridyl-4')naphthalene-1-carboxylic acid (B). Therefore, it may be assumed that oxidation of III in an alkaline medium yields salts of o-(2,3(CO),6,5(CO)-dibenzoylenisonicotinoyl)benzoic acid (IV). The same acid (IV) separated upon acidification of these solutions. It is characteristic that acid IV, like acid B, is rather easily decarboxylated; we shall report on this in a separate communication.



(A) (B)

The analogy between III and A extends to reactions with sodium alcoholates, which cleave the five-membered indanedione ring. It is interesting to note that, similarly to the case reported in reference [2], derivatives of dihydropyridine are not obtained in this case either; rather, pyridine derivatives – esters of o-(2,3(CO),6,5(CO)-dibenzoylenisonicotinoyl)benzoic acid (V) – are formed immediately. The identical substance is also obtained from the silver salt of acid IV by the action of an alkyl halide. These esters (V) are very stable toward hydrolysis.



A certain difference in the behavior of III and A should be noted. Oxidation of III by hydrogen peroxide in alcoholic alkali proceeds very rapidly, and a yellow precipitate appears after a minute, while in the case of A ten hours are required at room temperature (the reaction rate depends to a considerable extent on the amount of water in the solution). Dihydropyridine III also reacts more rapidly with sodium alcoholates. Acid B readily dissolves both in bases and in sodium bicarbonate, but acid IV, as already indicated, is almost insoluble in these media; it dissolves better in a water–alcohol mixture to which has been added a small amount of a base.

We have previously carried out the oxidation of dihydropyridine III [1], but the structure corresponding to the dimer was erroneously assigned to the product.

EXPERIMENTAL

o-(2,3(CO),6,5(CO)-dibenzoylenisonicotinoyl)benzoic acid (IV). a) From hydroxytrisindanedione. A mixture of 8 g of the enol form of hydroxytrisindanedione and 24 g of ammonium acetate in 240 ml of glacial acetic acid was refluxed for 2 hr. After the mixture had cooled., the precipitate was separated and boiled with 75 ml of acetic acid. There remained 5 g of a yellow crystalline substance with an m. p. of 365-368°.

b) By oxidation of indanedione-1,3-spirol(2:4')-2',3'(CO),6'5'(CO)-dibenzoylenedihydropyridine (III). To a suspension of 2.15 g of III in 150 ml of methanol were added 15 ml of 10% sodium hydroxide and 10 ml of perhydrol. The reddish brown precipitate dissolved to yield a green solution, and after several minutes, a yellow precipitate of the sodium salt of acid IV separated. The salt was dissolved in aqueous alcohol (1:1) by the addition of one drop of base, and acid IV, m. p. 364° (from dioxane), separated when the solution was made acid. The yellow crystals did not dissolve in sodium bicarbonate solution. A mixture with the substance obtained in(a) melted without depression of the melting point.

Found %: N 3.45(a), 3.13(b). $C_{27}H_{13}O_5N$. Calculated %: N 3.25.

Sodium salt. A solution of IV was prepared by heating 0.5 g in 50 ml of aqueous alcohol to which had been added 1 ml of 1% NaOH, and the hot solution was filtered through a heated funnel. The fine yellow crystals melted at 390° (with decomposition).

Found %: N 3.39; Na 4.85. $C_{27}H_{12}O_5NNa$. Calculated %: N 3.09; Na 5.07.

Potassium salt. To a suspension of 0.5 g of III in 40 ml of ethanol were added 5 ml of 2% KOH and 3 ml of perhydrol. The yellow crystalline precipitate was separated on the following day; m. p. 360° (with decomposition). The crystals were soluble in water and in dilute alcohol.

Found %: N 2.76; K 8.06. $C_{27}H_{12}O_5NK$. Calculated %: N 2.98; K 8.33.

Silver salt. To a hot solution of 0.1 g of the potassium salt in 70 ml of dilute alcohol (1:1) was slowly added an excess of $AgNO_3$ solution. The resulting yellow precipitate was soluble in hot $Na_2S_2O_3$ solutions and in dilute ammonia. We were unable to purify the salt.

Found %: N 2.85; Ag 16.9. $C_{27}H_{12}O_5NAg$. Calculated %: N 2.60; Ag 20.1.

Diethylamine salt. This salt was prepared similarly to the sodium or potassium salt. The yellow crystals melted at 340° (from dioxane).

Found %: N 5.54. $C_{31}H_{24}O_5N_2$. Calculated %: N 5.55.

Piperidine salt. Acid IV and piperidine were refluxed in ethanol, and the precipitate was added to boiling dioxane. The undissolved fine yellow needles melted at 326°.

Found %: N 5.54. $C_{32}H_{24}O_5N_2$. Calculated %: N 5.42.

β-Phenylisopropylamine salt. A mixture of 0.2 g of III, 2 ml of β-phenylisopropylamine, and 2 ml of perhydrol in 20 ml of methanol was refluxed for 2 hr. The yellow crystals melted at 263° (from dioxane).

Found %: N 4.74. $C_{36}H_{26}O_5N_2$. Calculated %: N 4.94.

Acid chloride of IV. A mixture of 5.8 g of carefully ground acid IV and 50 ml of thionyl chloride was refluxed for 3 hr. The acid was converted to the acid chloride, a yellow, finely crystalline precipitate; m. p. 335°.

Found %: N 3.08; Cl 7.90. $C_{27}H_{12}O_4NCl$. Calculated %: N 3.11; Cl 7.88.

Ethyl ester of acid IV. a) A mixture of 0.1 g of the silver salt of acid IV and 6 ml of ethyl iodide was heated in a sealed tube at 180° for 6 hr. The sealed tube was opened, and the ethyl iodide was vaporized. The residue was treated with 2% ammonia and crystallized from glacial acetic acid, m. p. 325-327°.

b) A mixture of 0.3 g of III and 25 ml of 1% sodium ethylate was allowed to stand overnight. The yellow precipitate was twice crystallized from glacial acetic acid. The fine needles (Vb) melted at 322-325°. A mixture with the ester prepared in(a) melted without depression of the melting point.

Found %: N 2.85(a), 2.92(b). $C_{29}H_{17}O_5N$. Calculated %: N 3.05.

Methyl ester of acid IV. A mixture of 0.3 g of III and 20 ml of 3% sodium methylate was boiled on a water bath for 10 minutes. The yellow precipitate (Va) was crystallized from glacial acetic acid; m. p. 338°.

Found %: N 3.08. $C_{28}H_{15}O_5N$. Calculated %: N 3.15.

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ABSORPTION SPECTRA OF DIPHENYLMETHANE AND DIPHENYLETHANE DERIVATIVES CONTAINING NITRO AND AMINO GROUPS ON DIFFERENT RINGS

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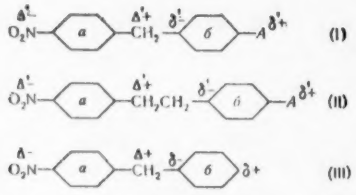
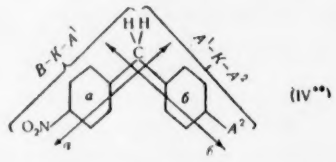
Original article submitted March 21, 1961

We have undertaken a study of the absorption spectra of compounds having structures represented by $O_2NPh\cdot(CH_2)_nPhA$.* Spectra have been obtained for derivatives of p-NO_2-diphenylmethane (p-NO_2-DPhM) (I) and p-NO_2-diphenylethane (p-NO_2-DPhE) (II) in which the electron donating chromophore component A^2 is H, $NHCOCH_3$, OH, NH_2, or NMe_2** (see Table 1 for color). Compounds (II) were prepared similarly to (I) [1].


(I)

(II)

(III)


(IV**)

Analysis of the spectra of the p-NO_2-DPhM compounds (I) was carried out from the point of view of the theory of inductively coupled systems [2, 3], which was developed for the analysis of spectra of diphenylamine derivatives having the structure 4-$O_2NPhNHPhA$-4'.

For derivatives of 4-NO_2-diphenylamine the basic chromophore system is the BKA' system O_2NPhNH, while for the p-NO_2PhM and p-NO_2-PhE derivatives the basic chromophore system must be the BKA' system p-O_2NPhCH_2 (IV), the state of which is modified by inductive coupling with the system KA^2. That such a course is correct is confirmed by the fact that we find in the spectra of (I) and (II) bands due to the systems associated with each nucleus; for nucleus a the system is BKA' (I^a and II^a bands), while for nucleus b it is KA^2, more accurately $A'KA^2$ (I^b and II^b bands) (see Table 1).

With the introduction of a phenyl group into O_2NPhCH_3 (No. 1), we observe a shift in the I^a band + 3 mμ and shift in the II^a band of + 10 mμ. The bathochromic shifts of the I^a and II^a bands on the basis of the calculated sum of the extinctions of the systems of the a and b nuclei are also + 3 mμ and + 10 mμ, respectively (No. 4), but the absorption limit at log ε = 1 is shifted by + 15 mμ (Nos. 1-4, Table 1, Fig. 1). In agreement with [3, 5], we consider this effect to be a consequence of an increase in polarization in the ground state of the BKA' system, O_2NPhCH_2; as a result of mutual induction, there arises a δ − in (III) which increases the Δ+ as compared to the Δ+ in the original O_2PhCH_3. That this approach is correct is confirmed by: 1) the fact that the curve of $O_2NPhCH_2CH_2Ph$ (No. 5) almost coincides with the curve for No. 1 (Fig. 2); replacement of the CH_2 group by a CH_2CH_2 leads to a decrease in the polarization of nucleus b, to a decrease in the inductive coupling, and to the approach of the spectrum to the calculated curve (Nos. 4 and 5); 2) the fact that a shift to a longer wavelength occurs with the introduction into (I) and (II) of $A^2 = NH_2$ and NMe_2.

* Ph = p-phenylene, C_6H_4, or C_6H_5 at the end of a chain; Me = CH_3; n = 1 or 2.

** Construction of scheme (IV) taking into account standard dimensions demonstrates the presence of steric factors hindering coplanarity of benzene nuclei a and b; according to [4], the rings are tilted 52°, and the angle between the vectors a and b is 120°.

No.	Compound (m. p. and color)	Solvent**	Bands of system of nucleus b: I^b λ_{max}	I^b ϵ_{max}	II^b λ_{max}	II^b ϵ_{max}	Bands of system of nucleus a: I^a λ_{max}	I^a ϵ_{max}	II^a λ_{max}	II^a ϵ_{max}	Exoband λ_{max}	Exoband ϵ_{max}	Absorption limits at log ϵ = 1
1	O_2NPhCH_3	A	–	–	–	–	274	10850	~320	830	–	–	385
2	O_2NPhCH_2Ph	A	–	–	–	–	277	10600	~330	820	–	–	400
2a	31° colorless	B	–	–	–	–	277	10400	~330	500	–	–	385
2b		H	–	–	–	–	267	11300	~310	330	–	–	385
3	H_3CPh	A	–	–	255 262	360 340	–	–	–	–	–	–	–
4	(O_2NPhCH_3 + H_3CPh) calc.	A	–	–	–	–	274	10800	~320	830	–	–	385
5	$O_2NPhCH_2CH_2Ph$	A	–	–	–	–	277	8200	~330	450	–	–	385
5a	70-71°, colorless	H	–	–	–	–	267	14000	~370	470	–	–	–
6	$O_2NPhCH_2PhNH_2$	A	235	11600	–	–	275	9200	~330	1530	~420	40	440
6a	98°, orange-yellow	B	–	–	–	–	275	8100	~320	1760	~420	20	435
6b		H	230	9680	–	–	255	14700	~320	1700	–	–	400
7	$H_3COPhNH_2$	A	235	11700	290	1800	–	–	–	–	–	–	–
8	(O_2NPhCH_3 + + H_3CPhNH_2) calc.	A	235	15900	–	–	274	11800	~320	900	–	–	385
9	$O_2NPhCH_2PhNH_2$	An, 10^{-2}	–	–	–	–	–	–	330	2640	~420	140	490
10	$O_2NPhCH_2CH_2PhNH_2$		235	12800	–	–	275	13400	~330	1100	420	135	475
10a	138°, yellow-orange	H	–	–	–	–	255	19200	~330	730	~400	130	437
11		An, 10^{-2}	–	–	–	–	–	–	~330	2700	~420	270	508
12	$O_2NPhCH_2PhNMe_2$		265	25200	–	–	~270	20000	~340	2235	~420	190	480
12a	87°, yellow-orange	B	–	–	–	–	~270	18900	~340	1600	~420	100	438
12b		H	262	25700	~302	4000	–	–	~340	1600	–	–	409
13	$H_3CPhNMe_2$	A	252	13300	302	1900	–	–	–	–	–	–	–
14	$O_2NPhCH_2PhNMe_2$	DMA	–	–	–	–	–	–	~340	3400	~420	670	500
15	(O_2NPhCH_3 + + $H_3CPhNMe_2$) calc.	A	252	19000	–	–	~270	13900	~330	800	–	–	385
		A	260	19500	–	–	~275	14400	~340	1100	430	250	515
	$O_2NPhCH_2\cdot$	H	260	20600	~302	3480	–	–	~340	750	~400	170	504
16	$\cdot CH_2PhNMe_2$	DMA	–	–	–	–	–	–	~340	3400	430	830	530
16a	174°, yellow-orange												

*The compound and solution numbers shown in the table correspond to the numbers in the text and figures. Concentration of the solutions was 10^{-4} mole/liter.

**A = alcohol, B = benzene, H = n-hexane, An = aniline, DMA = dimethylaniline.

Under the influence of A^2 there must arise in (I) a larger $\delta'-$ charge than the $\delta-$ in (III), which, in turn, should increase the polarization in BKA' ($\Delta' + > \Delta +$), and, in accordance with the rule connecting a bathochromic effect with the extent of electron shifting in the ground state [2, 5, 6], the spectrum should shift toward the red. The effect of NH_2 as A^2 in No. 6 on (I) λ^{IIa}_{max} is still small; λ^{IIa}_{max} remained at about 330 mμ, but ϵ^{IIa}_{max} increased to 1530 (Nos. 1, 2, and 6). However, there was a strong bathochromic shift of the absorption limit for No. 6; at log ϵ = 1 + 40 and +55 mμ as compared to No. 2 and No. 1 (Fig. 1), and a new band appeared as a break at about 420 mμ.

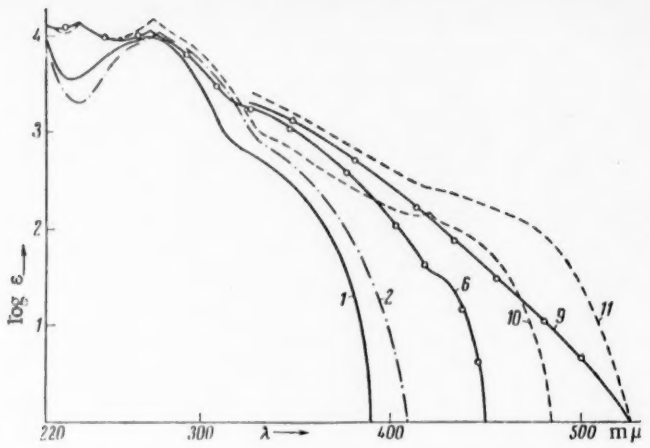


Fig. 1.

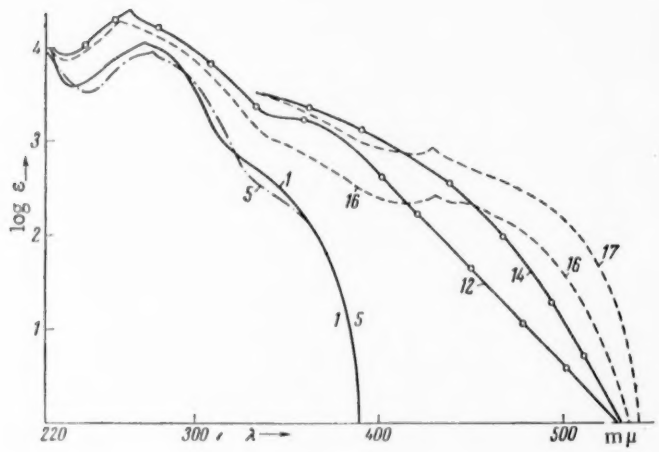


Fig. 2.

This is a consequence not of an endomolecular interaction, but of an exomolecular interaction of the external field of the electrophilic BKA' system O_2NPhCH_2 with the electron-donor $A'KA^2$ system CH_2PhNH_2 (IV) with the formation of a donor – acceptor complex by association (cf. the analogous association in reference [7]).

The presence of exomolecular interaction in solution No. 6 is confirmed by the increase in the bathochromic shift of the spectral curve in the exoband region with 1) an increase in concentration from $C = 10^{-4}$ to $C = 10^{-2}$ mole/liter; 2) with a passage from CH_2 to CH_2CH_2, i.e., to DPhE derivative No. 10; 3) with the addition to the alcoholic solution of an excess of the $A'KA^2$ component in the form of CH_3PhNH_2 or $C_6H_5NH_2$ (No. 9, Fig. 1, Table 1); 4) for spectrum No. 10 in aniline (No. 11, Fig. 1). This conclusion is confirmed by the significantly stronger endoeffect and exoeffect for (I, $A^2 = NMe_2$). Since NMe_2 is stronger than NH_2 (No. 12, Table 1, Fig. 2), the II^a band was shifted bathocromically by +10 mμ and was considerably more intense, and for the exoband the shift in the absorption limit at $\log \epsilon = 1$ was +95 and +80 mμ with respect to Nos. 1 and 2. That this effect is the consequence of the emergence of the exoband as a result of exomolecular interaction of the same type as the interaction in donor-acceptor complexes of nitro compounds with arylamines is shown by the greater shifts exhibited by Nos. 12 and 14 than Nos. 6 and 9 and than spectrum No. 15, which was calculated for the sum of the components (O_2NPhCH_3 + CH_3PhNMe_2); it is also shown by the fact that the DPhE derivative (II, $A^2 = NMe_2$) exhibited a clearly expressed exoband maximum, $\lambda_{max}^{exo} = 430$ mμ ($\epsilon = 250$), in spite of the low concentration, $C = 10^{-4}$ mole/liter; finally, it is shown by the increase in ϵ_{max} of the exoband of solution No. 17 in $C_6H_5NMe_2$ to 800 (Fig. 2) with a shift in the

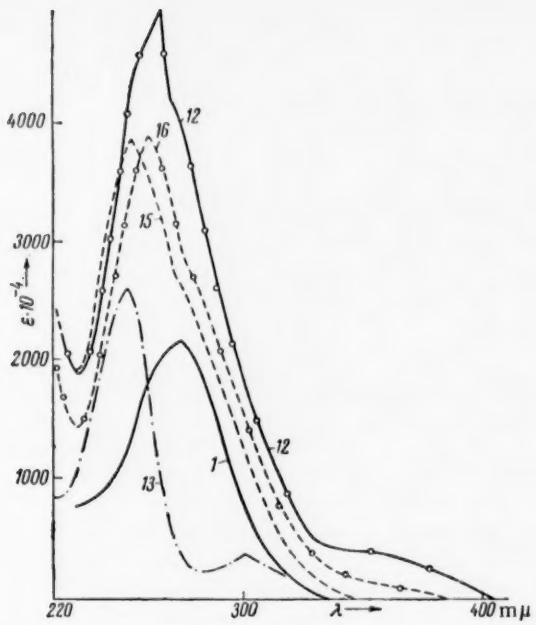
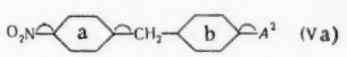


Fig. 3.

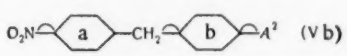
absorption limit at log ϵ = 1 by +130 mμ and +145 mμ with respect to Nos. 2 and 1 (Table 1) (i.e., when component KA^2 is present in excess so that there is a shift in the equilibrium toward a higher concentration of the complex).

It is apparent (Table 1, Fig. 3) that in the spectrum of No. 12, $O_2NPhCH_2PhNMe_2$, in the regions of bands I^a and II^a there is a significant deviation from curve No. 15, which was calculated for the sum of the components, and a still greater deviation from Nos. 1 and 2. This indicates a significant effect of mutual endomolecular influences of the NMe_2 and and NO_2 group; λ^{Ib}_{max} for No. 15 (252 mμ) is shifted toward the red by +13 mμ as compared to No. 12 with a significant increase in ϵ from 19000 to 25200. This effect is less for No. 16 ($\Delta\lambda$ + 8 mμ and ϵ_{max} is 19500); i.e., in No. 16 the endomolecular interaction is weaker. As a result of the greater separation of charges Δ^{+} from δ^{+} in (II), polarization of the system of nucleus a decreases.

Since in p-NO_2-DPhM the planes of the two nuclei a and b are tilted by 52° [4], and conditions for conjugation through the CH_2 group are disrupted. As a consequence of this, the CH_2 group can interact first with nucleus a and then with nucleus b depending on the rotation of the benzene nuclei. This can be explained by the existence of two rotational states (conformations), and can be represented by schemes (Va) and (Vb) with different positions for conjugation of the CH_2 with the nuclei a and b (σ, π conjugation). Owing to the opposite polarities of NO_2 and CH_2, position (Va) is favored (greater conjugation energy) and therefore predominates.



(Va)



(Vb)

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HYDROGENATION OF α-KETO ACIDS OVER COLLOIDAL PALLADIUM CATALYST

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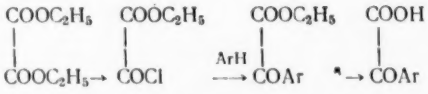
The study of asymmetric catalysis using catalysts supported on optically active carriers makes it possible to determine the correspondence between the asymmetric molecule formed during the reaction and the structure of the optically active compound used as the carrier. The previously discovered fact that asymmetric catalysis can be carried out with Skita's catalyst [1] permits an estimate of the steric interaction of the colloidal metal particles of the catalyst with the molecules of the lyophilic protective colloid. An essential factor is the formation of such colloidal asymmetric catalysts is the presence of structural entities formed by the molecules of the optically active protective colloid with the metal particles of the catalyst, on the one hand, and with the reacting molecules, on the other. Thus, the protective colloid fulfills the function of an asymmetric carrier, which is responsible for the occurrence of asymmetric catalysis [2]. This follows both from the fact that asymmetric catalysis does take place over such a catalyst [1] and from the fact that the hydrogenation of α-keto acids with the formation of α-hydroxy acids takes place in the kinetic region in the initial stage of the reaction. If a protective layer of the lyophilic colloid on the surface of the Pd particle were the determining factor in the formation of colloidal catalyst particles rather than a structural three-dimensional network of the macromolecule of the carrier combined with the colloidal metal particle [3], then diffusion factors would play a decisive role in the kinetics.

We have studied the kinetics of the hydrogenation of α-keto acids. Up to the present time, little attention has been given to the catalytic hydrogenation of α-keto acids. The work of Kindler et al. [4], who hydrogenated phenylglyoxylic acid and its esters for purposes of synthesis, is well known.

Hydrogenation of the keto acids was carried out in an alcohol – water medium at atmospheric pressure over the temperature interval of 5 to 40°. The apparatus consisted of a rocker bomb thermostatted to (± 0.1°). The colloidal palladium catalyst was prepared using gum arabic as the protective colloid with a palladium – colloid ratio of 1:2.3 (by weight). The gum arabic was freed from salts by a preliminary electrolysis (1000 v, 100 ma) over a period of 48 hr; it was then dried under vacuum. It had the following rotation: $[\alpha]^{20}D = -29.9°$ ($\alpha^{20}D = -1.67°$, c = 2.866, l = 1.9009, water). The catalyst was prepared by the method described in [5-7].

The α-keto acids were prepared by the method of [8]:



The α-keto acids were freed from possible catalyst poisons by agitation of their alcoholic solutions with skeletal nickel catalyst (1 hr, 10°, 10% Ni based on the keto acid); they were then recrystallized. The phenylglyoxylic acid had an m. p. of 64° (from CCl_4, xylene); the α-naphthylglyoxylic acid (separated from the beta isomer through the picrate) had an m. p. of 112-113° (from xylene).

The phenylglyoxylic acid was hydrogenated in an alcohol–water mixture having a ratio of 1:2; the alcohol–water medium used with the β-naphthylglyoxylic acid had a ratio of 1:1. The initial amount of acid was 0.005 mole. The rocker was operated at 800 oscillations per minute (20-cm stroke length). Special experiments established that the hydrogenation rate did not increase with an increase in rocker speed above 600 oscillations per minute.

The results obtained in the hydrogenation of the α-keto acids are presented in the figures. Figures 1 and 2 show the course of the hydrogenation of phenylglyoxylic, α-naphthylglyoxylic, and, for comparison, cinnamic acid.

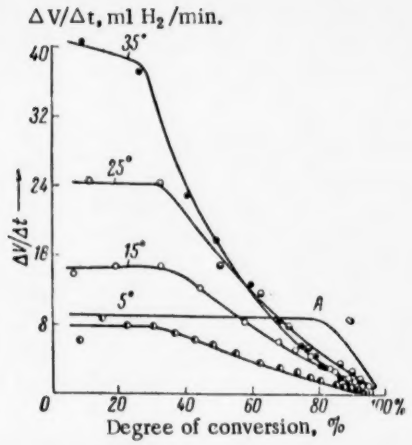


Fig. 1. Dependence of the rate of hydrogenation of phenylglyoxylic acid on the degree of conversion over the temperature interval 5-35° (10 mg palladium; 5 mM acid). (Curve A – hydrogenation of cinnamic acid at 25°).

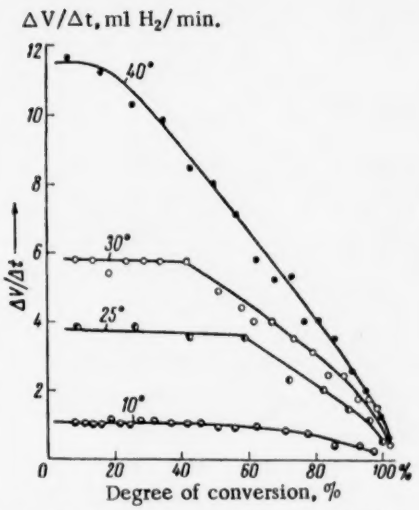


Fig. 2. Dependence of the rate of hydrogenation of α-naphthylglyoxylic acid on the degree of conversion over the temperature interval 10-40°.

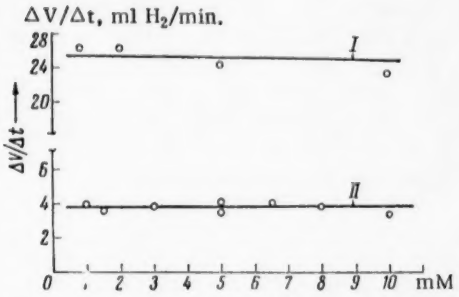


Fig. 3. Dependence of hydrogenation rate on the initial concentration of acid, 25°; 10 mg Pd: I) phenylglyoxylic acid; II) α-naphthylglyoxylic acid.

The graphs were constructed by plotting the rate [milliliters of H_2 absorbed (s.t.p.) per minute] against the degree of conversion (in percent).

As is apparent from Figs. 1 and 2, hydrogenation of the keto acids is zero order for 30-60% conversion, and then the reaction rate drops sharply. The change in the order of the reaction from zero to first order is in accordance with the hydrogenation theory discussed in [9]. That such a change takes place at low conversions is due to the strong adsorption of the reaction product (the α-hydroxy acid). This is not observed, for example, during hydrogenation of ethylenic and acetylenic compounds over colloidal palladium [6].

Taking as the rate constant the rate of absorption of hydrogen during 30-50% of the hydrogenation and varying the amount of the keto acid (by a factor of 6-8) at constant temperature (25°) and constant amount of catalyst (10 mg Pd), we obtained the straight lines shown in Fig. 3, where the rate [milliliters H_2 (s.t.p.) per minute] is plotted against the amount of hydrogenatable compound (in millimoles). The data confirm that the reaction was zero order with respect to the substance hydrogenated for the α-keto acids investigated. Investigation of the dependence of the rate of hydrogenation of the acid on the amount of catalyst (change in the amount of catalyst by a factor of 8-10) showed that the reaction is first order with respect to the catalyst, which indicates that the reaction takes place in the kinetic range and not in the surface diffusion region.

In Fig. 4 is shown the dependence of the rate of hydrogenation of phenylglyoxylic acid and of α-naphthylglyoxylic acid on the amount of catalyst (from 2 to 10 mg of Pd) at constant concentration of the hydrogenatable compound. It should be noted that for the acid not purified by prior catalyst treatment there was a limiting minimum concentration of catalyst (0.8-1.0 mg Pd per 0.003-0.005 mole of acid) below which reaction did not take place. This is explained by poisoning of small amounts of catalyst [11]. For the acid samples purified by precontacting, the relationship between rate and amount of catalyst was linear, and the lines passed through the origin (curves I and II, Fig. 4). First order kinetics with respect to the catalyst and zero order with respect to the hydrogenatable compound have been found for the hydrogenation of nitro compounds over colloidal palladium [12].

The temperature dependence of the rate of hydrogenation of α-keto acids is shown in Figs. 1 and 2. The rate of absorption of hydrogen in the region corresponding to zero order was taken as the rate constant. Arrhenium plots of the data were made, and the energies of activation were found to be 9.0 kcal/mole ($\varepsilon/\log k_0 = 1.99 \cdot 10^3$) for α-naphthylglyoxylic acid.

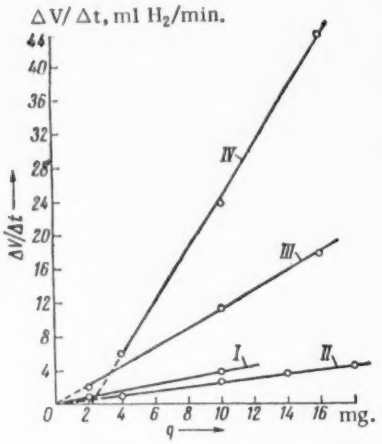


Fig. 4. Dependence of the rate of hydrogenation of α-keto acids on the amount of catalyst. I) α-Naphthylglyoxylic acid (25°, 5 mM); II) α-naphthylglyoxylic acid not purified by prior catalytic treatment (25°, 3 mM); III) α-naphthylglyoxylic acid (40°, 3 mM); IV) phenylglyoxylic acid (25°, 5 mM).

The data obtained on the hydrogenation kinetics of α-keto acids are of interest in understanding the fine structure of the colloidal catalyst. The mechanism by which the metal sols are protected is explainable to a significant extent by the presence of structural networks formed between hydrophobic and hydrophilic sols [3, 13]. Separate units (predominantly functional groups) of the macromolecule of the protective colloid are adsorbed on the surface of the metal particles, and their configuration is intermediate between a "Langmuir barrier" and a planar arrangement, and it approximates the shape of a W [14]. Owing to this, part of the catalyst surface remains free, and the catalytic reaction takes place on these portions (more precisely, on the zones of metal–carrier separation. The occurrence of the hydrogenation reaction in the kinetic region is due to these areas on the catalyst surface, and a transfer to the surface diffusion region was not noted even at an elevated temperature (40°) and high hydrogen-absorption rate (hydrogenation of phenylglyoxylic acid).

An increase in temperature promotes rupture of the structural network, thereby causing coagulation of the colloidal metal. In the case of colloidal catalysts, this must be accompanied by a decrease in the reaction rate and an increase in the role of diffusion factors in the kinetic region. Over the temperature range investigated (up to 40°), we did not observe a decrease in rate due to diffusion factors, as may be seen from the curve showing the relationship between reaction rate at 40° and amount of catalyst (curve III, Fig. 4). Consequently, coagulation of the catalysts did not occur to an appreciable extent during the course of the experiments.

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CONVERSION OF ISOPROPENYLCYCLOPROPANE IN THE PRESENCE OF KIESELGUHR

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Original article submitted April 3, 1961

We have previously shown that a number of catalysts promote rupture of the three-membered ring of alkylcyclopropanes at bonds attached to substituted carbon atoms, thereby forming olefins with an open chain [1, 2]. The first attempt to study the behavior under these conditions of cyclopropane hydrocarbons in which the ring is conjugated with a double bond were unsuccessful, since the catalyst was completely poisoned by reaction products at the very beginning of the experiment [3].

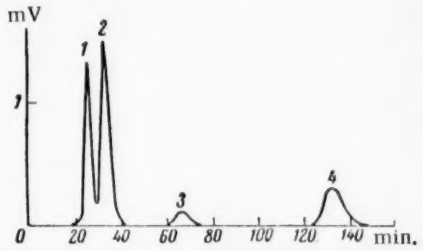

Fig. 1. Chromatogram of the synthetic mixture: 1) trans-2-methyl-1,3-pentadiene; 2) isopropenylcyclopropane; 3) cis-2-methyl-1,3-pentadiene; 4) 2-methyl-1,4-pentadiene.

In the present work, by carrying out short experiments and analyzing the catalyzates by gas–liuqid chromatography, we were able to study such conversions of isopropenylcyclopropane in somewhat more detail. It was found that alkylcyclopropanes and "conjugated" hydrocarbons of the cyclopropane series behave quite differently under the same conditions in the presence of kieselguhr. Thus, isopropylcyclopropane underwent 30% isomerization to olefins at 100°, and the weight of the catalyzate was the same as the weight of hydrocarbon charged. Under the same conditions (with a fresh portion of a catalyst) in a 30-minute experiment, isopropenylcyclopropane gave only a small amount of liquid catalyzate (8% of the original hydrocarbon) and more than 90% polymer, which remained on the catalyst.

The polymeric product was easily separated from the catalyst by extraction with n-pentane, and it was a thick, pale yellow tar with an agreeable pine odor. It is proposed to investigate the polymer in more detail in the future.

Analysis of the liquid catalyzates revealed that they contained unreacted isopropenylcyclopropane as well as all possible 2-methylpentadienes. The quantitative composition of the liquid reaction products is given in the experimental section, however, no special significance can be attached to these data, since kieselguhr can cause shifting of the double bonds in the dienes.

The formation of polymer which remained on the catalyst caused loss of catalyst activity; this became apparent when longer experiments were carried out. Thus, in a 200-minute experiment, the weight ratio of liquid catalyzate to polymer (polymer weight determined as weight increase of the catalyst) was not 8: 92, as in the 30-minute experiment, but 53: 47, and the total conversion of isopropenylcyclopropane did not exceed 70%, while it was 93% in the 30-minute experiment.

The presence of 2-methylpentadienes in the catalyzate can be explained by isomerization of the three-membered cyclopropane ring in accordance with the following scheme:

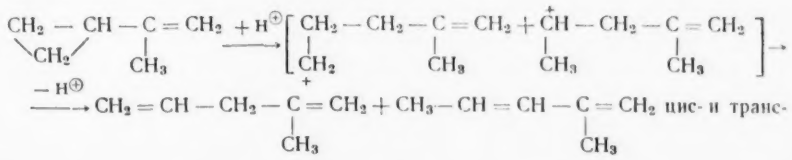

TABLE 1

Hydrocarbon	B. p., °C (760 mm)	$n^{20}D$	d^{20}_4
Isopropenylcyclopropane	70,3	1.4255	0.7513
	70,33*	1.42550*	0.75153*
Isopropylcyclopropane	58.2	1.3863	0.6981
	58.37*	1.38639*	0.69829*
2-Methyl-1,4-pentadiene	56.3	1.4057	0.6928
	56**	1.405**	0.694**
Cis- + trans-2-methyl-1,3-cyclopentadiene	75.5	1.4462	0.7207
	76**	1.446**	0.719**

* From [5].

** From [6].

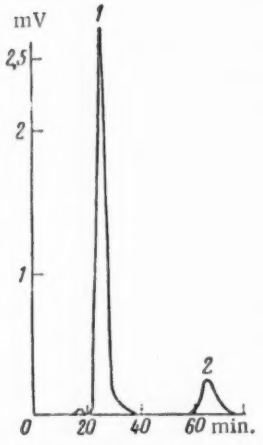

Fig. 2. Chromatogram of 2-methyl-1,3-pentadiene. 1) Trans-2-methyl-1,3-pentadiene; 2) cis-2-methyl-1,3-pentadiene.

The polymer – the major product of the conversion of isopropenylcyclopropane over kieselguhr – could have been formed either from the methyl-1,3-pentadienes, i.e., as a secondary reaction product or during an intermediate stage of the reaction prior to stabilization of the carbonium ion, which could be the initial center of polymerization. The experimental data obtained in the present work do not provide a sufficient basis on which to arrive at a final conclusion regarding the mechanism of the reaction. We therefore propose to continue these investigations. The fact that extensive polymerization occurred when the "conjugated" cyclopropane hydrocarbon was contacted with kieselguhr is, in our opinion, of considerable interest in its own right, since it is indicative of the increased reactivity of such systems.

1. Synthesis and properties of the hydrocarbons. The isopropenylcyclopropane was prepared by dehydration of dimethylcyclopropylcarbinol by a previously described method [4]. The isopropylcyclopropane was prepared by hydrogenation of the isopropenylcyclopropane in an autoclave at 100-130° over copper-chrome catalyst. The 2-methyl-1,4-pentadiene and the mixture of stereoisomeric 2-methyl-1,3-pentadienes (which were required as standards in the analysis of the catalyzates) were prepared by pyrolysis of the acetate of an unsaturated alcohol (synthesized from methallyl chloride and acetaldehyde) with subsequent distillation in a column.

2. Experimental method. The experiments were carried out by the method described previously [1]. "Kisatibl" kieselguhr was used as the catalyst, and it was given a preliminary heat treatment at 120° in a stream of nitrogen to remove the water. The amount of catalyst used was 10 ml. A new portion of catalyst was used in each experiment. In all experiments, the hydrocarbon was passed over the catalyst at a space rate of 0.2 $hours^{-1}$.

The liquid phase in the chromatographic analysis was a saturated solution of silver nitrate in glycerin [7, 8], and the solid phase was diatomaceous brick with a particle size of 0.25-0.5 mm. A thermal conductivity detector was used. The analysis was carried out at 40°. The rate of carrier gas (nitrogen) was 30 ml/minute at the inlet. Table 2 and Fig. 1 presents the results of a chromatographic determination of the composition of a synthetic mixture prepared from the hydrocarbons obtained as described above. The chromatogram of the mixture of 2-methyl-1,3-pentadienes is shown in Fig. 2. It shows that the mixture contained 89.3% trans isomer and 10.7% cis isomer.

3. Catalytic experiments. The data obtained during these experiments are shown in Table 3. The experiments were carried out at 100°. The data of Table 3 show that the conversion of isopropenylcyclopropane was considerably more extensive than that of isopropylcyclopropane. In the case of isopropenylcyclopropane, the weight of the catalyzate did not correspond to the weight of the original hydrocarbon, since a part of the product remaining dropped with an increase in time as a consequence of poisoning of the catalyst.

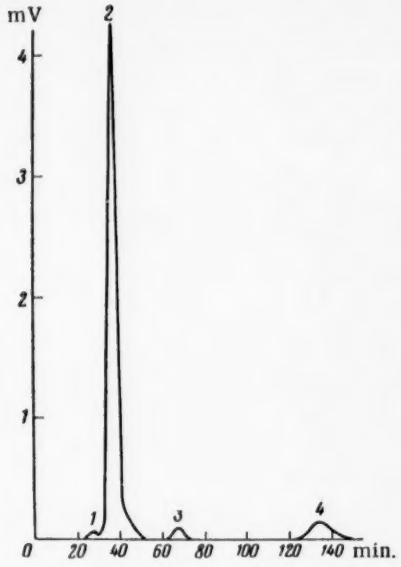

Fig. 3. Chromatogram of the catalyzate obtained during conversion of isopropenylcyclopropane at 100°. 1) Trans 2-methyl-1,3-pentadiene; 2) isopropenylcyclopropane; 3) cis-2-methyl-1,3-pentadiene; 4) 2-methyl-1,4-cyclopentadiene.

TABLE 2

Hydrocarbon	Known comp., wt. %	From chromatog., wt. %
2-Methyl-1,3-pentadiene		
trans	36.2	32.6
cis		4.2
2-Methyl-1,4-pentadiene	20.3	21.2
Isopropenylcyclopropane	43.5	42.1

The composition (in percent) of the liquid catalyzates obtained in experiments with isopropenylcyclopropane at different periods of catalyst operation and at different temperatures are shown in Table 4. These data show that the liquid catalyzates from all experiments contained various 2-methylpentadienes, and the ratios of the isomers varied with the time the catalyst had been in use with the reaction temperature. In addition to the 2-methyl-1,3- and 1,4-pentadienes, the catalyzate obtained at 150° contained an appreciable amount of an unidentified impurity. It may be assumed that this was 2-methyl-2,4-pentadiene, which was formed as a result of shifting of the double bond in 2-methyl-1,4-pentadiene.

The chromatogram of the catalyzate obtained at 100° is shown in Fig. 3.

TABLE 3

Hydrocarbon	Experiment length, min	Wt. hydrocarbon fed, g	Wt. catalyzate, g	Wt. incr. cat., g	Conv., %
Isopropylcyclopropane	60	1.70	1.70	–	30*
Isopropenylcyclopropane	30	0.75	0.07	0.69	93
Isopropenylcyclopropane	200	6.50	3.10	3.10	70.0

* Olefins produced in this experiment were determined by bromine number.

TABLE 4

Hydrocarbon	At 100°			At 50°
	first 30 minutes	second 30 minutes	200 minutes	30 minutes
Isopropenylcyclopropane	88.2	93.5	52.9	30.0
trans-2-Methyl-1,3-pentadiene	1.4	0.2	5.1	26.2
cis-2-Methyl-1,3-pentadiene	2.8	1.0	8.0	18.8
2-Methyl-1,4-pentadiene	7.1	4.6	34.0	20.5
Not identified	0.5	0.7	0.0	4.4

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REACTIONS OF DIBORANE AND ALKYLDIBORANES WITH ESTERS OF BORIC AND ALKANEBORONIC ACIDS AND THEIR THIO ANALOGS

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Original article submitted March 22, 1961

One of us and Dorokhov [1] found that diaryldiboranes and orthoborates are formed by the action of diborane on esters of diarylborinic acids.

In a continuation of the investigation of the reactions of diborane with organoboron compounds, we discovered that the interaction of diborane and esters of dialkylborinic acids at room temperature yields not the expected tetraalkyldiboranes and esters of boric acid but esters of alkaneboronic acids and tetraalkyldiboranes, which are obtained in good yields; these compounds are formed in accordance with the following equation:

$$8R_2BOR' + B_2H_6 \rightarrow 4RB(OR')_2 + 3(R_2BH)_2. \quad (1)$$

The mechanism of this reaction consists of a series of successive and parallel reactions including substitution of a hydrogen atom in the diborane or its derivatives by an alkoxy or alkyl radical.

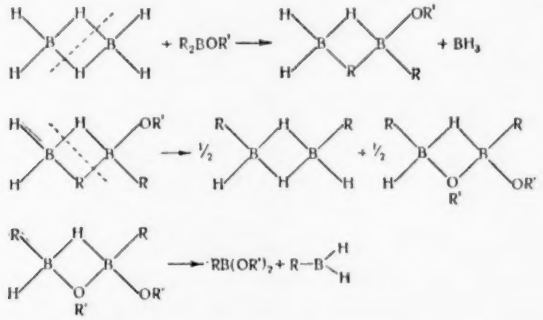
The first course of the initial stage of the reaction includes an exchange of a hydrogen atom in the diborane for an alkyl group, which results in the formation of an alkylalkoxyborine and an alkylborine:

$$R_2BOR' + BH_3 \rightarrow RB\begin{matrix}H\\OR'\end{matrix} + RBH_2. \quad (2)$$

The alkylalkoxyborine formed in accordance with Eq. (2) then disproportionates to an ester of an alkaneboronic acid and an alkylborine:

$$2RB\begin{matrix}H\\OR'\end{matrix} \rightarrow RB(OR')_2 + RBH_2. \quad (3)$$

Equations (2) and (3) are schematic representations of the processes. In actuality, these and all reactions considered below take place with the participation of dimeric molecules with three-center bonds formed by boron and hydrogen atoms and also by alkyl and alkoxy groups. Thus, Eq. (2) and (3) should be represented as follows:



The alkylborine formed by Eq. (3), as a compound containing a B—H bond, can, in turn, react with esters of dialkylborinic acids, exchanging a hydrogen atom for an alkyl group:

$$R_2BOR' + RBH_2 \rightarrow RB\begin{matrix}H\\OR'\end{matrix} + R_2BH. \quad (4)$$

Thus, as a result of Eq. (4), a dialkylborine is obtained. This dimerizes to a tetraalkyldiborane and an alkylalkoxyborine, which is converted by Eq. (3) to an ester of an alkylborinic acid and an alkylborine.

The second course of the primary reaction includes an exchange of an alkoxy group in the dialkylborinic acid ester for a hydrogen atom, as a result of which a dialkylborine and an alkoxyborine are obtained:

$$R_2BOR' + BH_3 \rightarrow R_2BH + R'OBH_2. \quad (5)$$

The alkoxyborine can undergo various reactions. Thus, by reacting with esters of dialkylborinic acids, it is converted to an alkylalkoxyborine:

$$R_2BOR' + R'OBH_2 \rightarrow 2RB\begin{matrix}H\\OR'\end{matrix}, \quad (6)$$

and its reaction with a dialkylborine leads to an alkylborine and an alkylalkoxyborine:

$$R_2BH + R'OBH_2 \rightarrow RBH_2 + RB\begin{matrix}H\\OR'\end{matrix} \quad (7)$$

Moreover, alkoxyborines can decompose to orthoborates and diborane (through a stage in which a dialkoxyborine is formed) [2] in accordance with the following equation:

$$R'OBH_2 \rightarrow {}^1/_3\,(R'O)_3B + {}^2/_3BH_3. \quad (8)$$

Indeed in certain experiments, it was possible to isolate a small amount of orthoborates during distillation of the reaction products.

Consequently, in the final analysis, during this initial course of reaction (5), the process is completed with the formation of the same final products, since the alkylborines and alkylalkoxyborines are further converted in accordance with Eqs. (3) and (4) to esters of alkaneboronic acids and to tetraalkyldiboranes.

Further, we investigated reactions of orthoborates with alkylborines. It was found that tetraalkyldiboranes, which we previously obtained from diborane and trialkylborines [3], react with orthoborates (slowly at room temperature and rapidly upon moderate heating, 60-100°) with the formation of esters of alkaneboronic acids in yields of abour 80%, in accordance with the following equation:

$$(R_2BH)_2 + 2\,(R'O)_3B \rightarrow 3RB\,(OR')_2 + {}^1/_2\,(RBH_2)_2. \quad (9)$$

The initial stage of this reaction is concluded with the exchange of a hydrogen atom in the tetraalkyldiborane for an alkoxy group:

$$R_2BH + (R'O)_3B \rightarrow R_2BOR' + (R'O)_2BH. \quad (10)$$

A second theoretically possible reaction — exchange of an alkyl group for an alkoxy group — is improbable, since, as is well known from investigations of reactions between trialkylborines and orthoborates [4, 5], similar reactions require a higher temperature (about 200°).

Further conversions of the esters of dialkylborinic acids and dialkoxyborines (10) are analogous to the conversions described by Eqs. (6)-(8) and (3)-(5). These reactions result in esters of alkaneboronic acids and alkylborines. All of the reactions discussed above are reversible. Reaction (1), for example, can be shifted in the direction of the

formation of the dialkylborinic acid ester by removing the diborane from the reaction mixture. Thus, when tetra-n-propyldiborane and n-propaneboronic acid dimethyl ester were refluxed for 4 hr, about 50% diborane was evolved, and distillation of the reaction products, which had been given a preliminary treatment with aniline, gave the same yield of di-n-propylboronic acid methyl ester:

$$3(R_2BH)_2 + 4RB(OR')_2 \rightleftarrows 8R_2BOR' + B_2H_6,$$
$$R = n\text{-}C_3H_7;\ R' = CH_3. \quad (11)$$

The conversion of dialkyldiboranes to diborane and tetraalkyldiboranes is also reversible:

$$2R_2B_2H_4 \rightleftarrows R_4B_2H_2 + B_2H_6. \quad (12)$$

Therefore, when a tetralkyldiborane and an orthoborate are heated at the boiling point, the reaction does not proceed by Eq. (9), but in accordance with the following equation:

$$3(R_2BH)_2 + 8(R'O)_3B \rightarrow 12RB(OR')_2 + B_2H_6. \quad (13)$$

Thus, when tetra-n-propyldiborane and methyl borate was refluxed for 2 hr, 100% of the diborane calculated by Eq. (13) was evolved, and distillation of the reaction products gave the dimethyl ester of n-propaneboronic acid in 80% yield.

We also found that dialkyldiboranes react with trialkylborines with the formation of tetraalkyldiboranes. This suggested the possibility of carrying out certain interesting reactions between trialkylborines and orthoborates or esters of alkaneboronic acids in the presence of catalytic amounts of tetraalkyldiboranes. We have already reported one such reaction in a preliminary communication [6].

As we have previously stated, trialkylborines react slowly with orthoborates at a temperature of about 200° with the formation of esters of alkaneboronic or dialkylborinic acids depending on the nature of the alkyl group in the trialkylborine. When this reaction is carried out in the presence of catalytic amounts of a tetraalkyldiborane and with moderate heating (60-100°), the reaction proceeds rapidly with the formation of esters of alkaneboronic acids in high yields (70-90%):

$$R_3B + 2(R'O)_3B \xrightarrow{(R_2BH)_2} 3RB(OR')_2. \quad (14)$$

The reaction boils down to the interaction of the tetraalkyldiborane and orthoborate by reaction (9) and subsequent conversion of the resulting dialkyldiborane and the original trialkylborine to a tetraalkyldiborane. This is the route by which the tetraalkyldiborane is regenerated after catalyzing reaction (14). Esters of dialkylborinic acids can be converted by this same route in high yields (70-90%) to esters of alkaneboronic acids merely by heating them with orthoborates in the presence of a catalytic amount of a tetraalkyldiborane:

$$R_2BOR' + (R'O)_3B \xrightarrow{(R_2BH)_2} 2RB(OR')_2. \quad (15)$$

Here, also, the tetraalkyldiborane and orthoborate first form a dialkoxyborine, which, either directly (analogously to reactions (6) and (3) or through decomposition to diborane and an orthoborate, converts esters of dialkylborinic acids to esters of alkaneboronic acids [similarly to reactions (8) and (1)], whereupon the tetraalkyldiborane is regenerated.

Finally, it is possible under the influence of a small amount of a tetraalkyldiborane to convert an equimolar mixture of a trialkylborine and alkaneboronic acid ester to a dialkylborinic acid ester:

$$R_3B + RB(OR')_2 \xrightarrow{(R_2BH)_2} 2R_2BOR' \quad (16)$$

(the yield of dialkylborinic acid ester is 50-70%).

It should be remarked that reactions (15) and (16) [and also (1)] are still the only methods for the conversion of esters of dialkylborinic acids to esters of alkaneboronic acids and the reverse. Thus, it is now possible easily and simply to prepare esters of alkaneboronic and dialkylborinic acids from olefins, diborane, and alcohols and to convert each into the other.

The thio analogs of orthoborates and of esters of alkaneboronic and dialkylborinic acids behave in a similar manner. Thus, by heating tri-n-butyl thioborate and tri-n-butylborine at 130-140° for 2 hr in the presence of catalytic amounts of tetra-n-butyldiborane we obtained a 73% yield of n-butanethioboronic acid di-n-butyl ester. (17). A small amount of di-n-butylborinic acid n-butyl ester was formed as a by-product of the reaction.

$$2\,(RS)_3B + R_3B \xrightarrow{(R_2BH)_2} 3RB\,(SR)_2, \qquad (17)$$
$$R = n\text{-}C_4H_9.$$

It should be noted that this reaction requires the use of more vigorous conditions than in the case of the orthoborates. This is apparently connected with the fact that a hydrogen atom in the tetraalkylmercaptodiborane, which is formed in the first stage of the process [see (10) with the $(R'O)_3B$ replaced by an $(RS)_3B$], reacts with different reagents only at a temperature of about 100° [7]. On the strength of this, of course, exchange of a hydrogen atom in the tetraalkylmercaptodiborane for an alkyl group proceeds rather rapidly at temperatures of about 100° and above. It is possible that dialkoxyborines also only slowly exchange their hydrogen atom for an alkyl group at room temperature or upon moderate heating (60-100°). However, in contrast to tetraalkylmercaptodiboranes, dialkoxyborines are unstable compounds which easily decompose to diborane and an orthoborate (similarly to the reaction reported in [8]), and, therefore, in reactions in which dialkoxyborines take part at low temperatures and exchange a hydrogen atom for an alkyl group, it is not the dialkoxyborine itself but diborane which actually takes part in the reaction.

It may be remarked that all of the reactions discussed above in which a tetraalkyldiborane participates are very convenient and simple methods for preparative purposes. In carrying out the reaction, the mixture of reagents is heated with stirring for 1.5-2 hr on a boiling water bath (with the exception of reactions with thio derivatives, which proceed at the same rate at 130-140°) in the presence of 1% (molar) of a tetraalkyldiborane. The reaction mixture is then treated with alcohol or aniline to remove traces of alkylborines, and simple distillation results in high yields of esters of alkaneboronic or dialkylborinic acids.

Since the reactions are reversible, after separation of the major reaction product the process again shifts toward its formation. Thus, carrying out the process again with the intermediate fractions obtained during the fractionation and with the by-products yields the desired ester, so that the yield of ester approaches theoretical.

Not only tetraalkyldiboranes, but also diborane and its alkyl, alkoxy, and alkylmercapto derivatives have a catalytic effect on reactions (14), (15), and (16).

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ISOTOPE EXCHANGE BETWEEN SUBSTITUTED BENZYLMERCURY BROMIDES AND MERCURIC BROMIDE LABELED WITH THE RADIOACTIVE ISOTOPE Hg^{203}

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In connection with a study of the mechanism of electrophilic substitution at a saturated carbon atom, we recently investigated a number of examples of isotope exchange between organomercury salts and mercuric halides [1-6]:

$$R_1R_2R_3-HgX + X-Hg^{203}X \rightleftarrows R_1R_2R_3-Hg^{203}X + HgX_2.$$

The most thorough studies of isotope exchange were carried out with α-bromomercuryarylacetic acid esters (R_1 = Ar, R_2 = COOAlk, R_3 = H) and radioactive mercuric bromide [3, 6], since isotope exchange took place readily between these compounds.

The present paper describes the results of a study of the kinetics of isotope exchange between the simpler benzyl organomercury compounds (R_1 = Ar, $R_2 = R_3$ = H) and mercuric bromide labeled with the radioactive mercury isotope Hg^{203}.

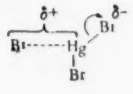
$$X-C_6H_4-CH_2-HgBr + Hg^{203}Br_2 \rightleftarrows X-C_6H_4-CH_2-Hg^{203}Br + HgBr_2.$$

It was first of all found that replacement of the carbalkoxy group by a hydrogen, i.e., a change from esters of α-bromomercuryarylacetic acids to benzylmercury bromide, leads to a significant decrease in the rate of isotope exchange.

In all of the solvents tested (toluene, bromobenzene, alcohol, acetone, dioxane, acetonitrile, N,N-dimethylformamide, glacial acetic acid, formic acid, isoamyl acetate, isoamyl ether, carbon tetrachloride, and pyridine), the reaction either takes place too slowly, or decomposition of the organomercury salt occurs. An exception is quinoline, in which isotope exchange takes place at 70° with a rate satisfactory for measuring the kinetics and without decomposition of the organomercury salt. Of course, under these conditions the mercuric bromide is at least partially present in the form of a complex with the quinoline.

Isotope exchange between benzylmercury bromide and mercuric bromide is a second order reaction overall, and is first order with respect to each of the components. Thus, it is a bimolecular electrophilic substitution reaction at a saturated carbon atom (S_E2). K_2 = 0.148 liters/mole/hour.

Apparently, it is not free mercuric bromide which reacts with the benzylmercury bromide, but its complex with quinoline (B:);* the molecules of this complex should be more polar than the molecules of mercuric bromide:



* The possibility cannot be excluded that the organomercury salt also takes part in the reaction in the form of the complex $R-HgX \cdot C_9H_7N$.

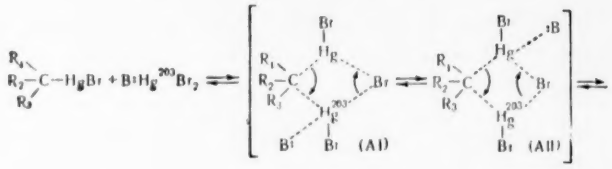
We have previously remarked repeatedly [1, 2] that the catalytic effect of a base on the rate of isotope exchange reactions of the type:

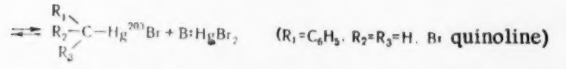
$$RHgX + Hg^{203}X_2 \rightleftarrows RHg^{203}X + HgX_2,$$

is apparently due, at least in part, to the fact that a complex of the base with the mercuric bromide ($B:HgX_2$) is a stronger electrophilic reagent than the slightly polar mercuric halide.

A second possible reason for the catalytic effect of the base is that the base solvates the mercury atom leaving the molecule of the organomercury compound.

Taking into account these assumptions, the mechanism of the isotope exchange reaction between benzylmercury bromide and mercuric bromide in quinoline can be represented as follows:*





The question remains open as to whether the molecule of base B transfers from the radioactive mercury atom to the nonradioactive atom inside the activated complex or whether the process (AI) → (AII) is a process in which the nonradioactive mercury atom leaves and is simultaneously solvated by the other molecule of the base. Of course, the question does not exist if it is a complex of a molecule of the organomercury salt with quinoline, $R_1R_2R_3{-}HgBr:B$, and not the uncomplexed molecule which takes part in the formation of the transition complex.

The energy of activation of this reaction proved to be 18.8 ± 0.9 kcal/mole. The rate constant K_2 was 0.066, 0.148, 0.323, and 0.641 liters·mole·hour at temperatures of, respectively, 60, 70, 80, and 88°.

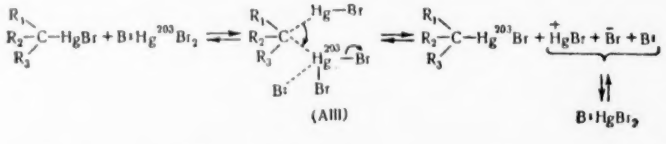
The effect of structural factors on the rate of this reaction was studied using a series of para-substituted benzylmercury bromides:

(X = F, Cl, H, CH_3, $(CH_3)_2CH$)

All reactions were carried out in quinoline medium** with equimolar concentrations of the reagents of $5.4 \cdot 10^{-2}$ mole/liter and at a temperature of 70°.

Solutions of the organomercury compound and mercuric bromide solutions were brought to the temperature of the experiment in a thermostatted system. The solutions were then poured together, and samples of the solution were taken from the reaction mixture at specific time intervals. The sample of the quinoline solution was then

* The cyclic transition complex represented in this scheme is more probable in reactions of this type with the least polar solvent. Since quinoline is not a nonpolar solvent, it is impossible to exclude the possibility of a noncyclic transition complex of the type (AIII):



** The quinoline was allowed to stand for a long time over solid potassium hydroxide, and it was distilled over zinc dust before each experiment. The fraction boiling at 118-119° at 20 mm Hg was collected.

$X-C_6H_4-CH_2-HgBr$

	Reaction time, t, hours	Activity of layer, imp./min.		Degree of isotope exchange, F	$-\lg(1-F)$	K_2, liters/mole/hour
		water	organic			
$X = (CH_3)_2CH$	10	2000	258	0,23	0,1135	
	15	1824	355	0,33	0,1739	
	20	1828	472	0,41	0,2291	0,237
	25	1709	538	0,48	0,2840	
	30	1611	635	0,56	0,3565	
	35	1474	642	0,61	0,4089	
	40	1440	707	0,68	0,4949	
	45	1408	755	0,70	0,5229	
	50	1459	880	0,75	0,6021	
	60	1256	837	0,80	0,6990	
$X = CH_3$	6	2217	183	0,15	0,0706	
	17	3317	653	0,33	0,1739	
	20	2741	594	0,36	0,1938	
	25	2489	678	0,43	0,2441	
	30	2711	905	0,50	0,3010	0,206
	35	2103	814	0,56	0,3565	
	40	2761	1185	0,60	0,3979	
	45	2082	919	0,61	0,4089	
	50	2208	1154	0,69	0,5086	
	55	2280	1182	0,68	0,4949	
$X = H$	10	2420	170	0,13	0,0605	
	20	2485	388	0,27	0,1376	
	30	1963	447	0,37	0,2007	
	42	2153	708	0,50	0,3010	
	50	1726	648	0,55	0,3468	0,148
	60	1743	798	0,63	0,4318	
	74	1496	827	0,71	0,5376	
	94	1331	856	0,78	0,6576	
$X = Cl$	10	2210	174	0,15	0,0706	
	20	2020	277	0,24	0,1192	
	30	1926	390	0,34	0,1938	
	40	1701	473	0,44	0,2518	0,131
	50	1616	558	0,51	0,3098	
	60	1453	587	0,58	0,3768	
	79	1304	678	0,68	0,4949	
$X = F$	6	2349	86	0,07	0,0315	
	20	3146	418	0,23	0,1135	
	25	3007	505	0,29	0,1487	
	30	2818	544	0,32	0,1675	
	35	2719	648	0,38	0,2076	0,121
	40	2241	573	0,41	0,2291	
	45	2572	732	0,44	0,2518	
	50	2631	811	0,47	0,2757	
	55	2673	962	0,53	0,3279	

diluted ten-fold with toluene, and this solution was treated with a saturated solution of sodium bromide in water to remove mercuric bromide. The aqueous layer, which contained the mercuric bromide, was separated from the organic layer, which contained the organomercury salt, and the activity of each layer was determined with a B-2 apparatus.

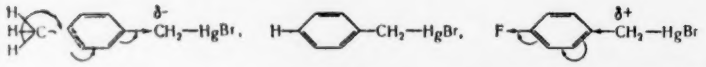
The isotope exchange results are shown in the table and figure.

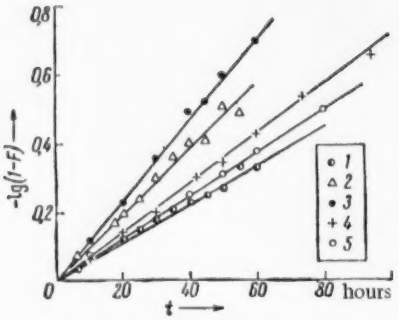
These results* show that the substituents, X, may be arranged in the following series with respect to their accelerating effect on the isotope exchange reaction (the half-life period of the reaction in hours is shown in parentheses):**

* Isotope exchange experiments carried out under the same conditions but at a different time gave results which reproduced the first results well; the straight lines of $\log(1-F) = f(t)$ for each of the organomercury compounds practically coincided, and the scatter of points for each line did not exceed ± 3% on the average.

** We note that the dependence of the rate of this reaction on the nature of the substituent X is the reverse of the dependence in the monomolecular isotope exchange reaction (S_E1) between ethyl α-bromomercuryphenylacetate and mercuric bromide, which was studied by one of us with V. I. Sokolov and I. P. Beletskaya [6].

$$\underset{(53)}{F} < \underset{(49)}{Cl} < \underset{(43)}{H} < \underset{(31)}{CH_3} < \underset{(27)}{(CH_3)_2CH}$$





Isotope exchange between $XC_6H_4CH_2HgBr$ and $Hg^{203}Br_2$ in quinoline at 70°. 1) p-$FC_6H_4CH_2HgBr$; 2) p-$CH_3C_6H_4CH_2HgBr$; 3) p-iso-$C_3H_7C_6H_4CH_2HgBr$; 4) $C_6H_5CH_2HgBr$; 5) p-$ClC_6H_4CH_2HgBr$.

The observed dependence of the rate of this S_E2 reaction on the nature of the substituent X is quite understandable; the effect of electronegative substituents is expressed in the appearance at the carbon atom bonded to the mercury atom of a partial negative charge, while the effect of an electropositive substituent is to place a partial positive charge at this carbon (apparently chiefly at the moment of reaction) as compared to the unsubstituted benzylmercurybromide.

In the first case, the attack of the organomercury compound on the electrophilic complex, $B{:}\,HgBr_2$, is facilitated, while in the second it is hindered.

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METAL DIALKYL DITHIOPHOSPHATE ANTIOXIDANTS

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It has been shown in previous work that certain derivatives of dithiophosphoric acid, specifically, the metal dialkyl dithiophosphates, are polyfunctional additives for lubricating oils [1, 2]. Additives of this type possess detergent, anticorrosion, and antiwear properties; with an appropriate structure, they also serve as foam suppressors and de-emulsifiers.

The present paper presents the results of an investigation of metal dialkyl dithiophosphates as antioxidants for the hydrocarbons in lubricating oils. The comparative antioxidant activity of metal dialkyl dithiophosphates of different structures was studied, and the effect of certain factors on the oxidation of hydrocarbons in the presence of these additives was demonstrated.

Additives having the structures shown in the table were synthesized for this investigation.

Structures of the Dialkyl Dithiophosphate Additives

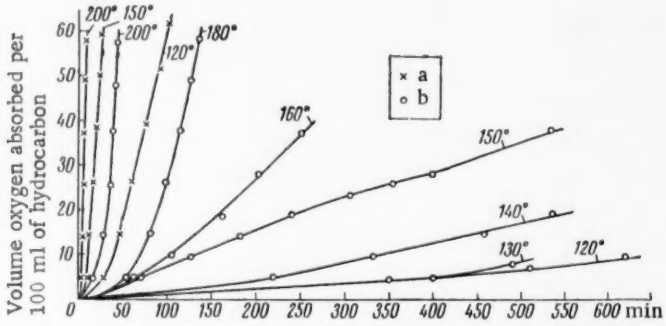
Additive designation	Formula
DF-1	$[(RO)_2PSS]_2Ba$, $R = C_{20} - C_{24}$
DF-2	$[(RO)_2PSS]_2Ba$, $R = C_{16} - C_{20}$
DF-12	$[(CH_3(CH_2)_3CH\,CH_2O)_2\,PSS]_2\,Ba$ (with C_2H_5)
DF-5	$[(RO)_2PSS]_2Zn$, $R = C_{20} - C_{24}$
DF-8	$[(CH_3\,(CH_2)_5\,CHO)_2\,PSS]_2\,Zn$ (with CH_3)
DF-9	$[(CH_3\,(CH_2)_3CH\,CH_2O)_2PSS]_2Zn$ (with C_2H_5)
DF-10	$[CH_3\,(CH_2)_5CHO]_2\,PSSZnSSP\,[OCH_2\,CH\,(CH_3)_2]_2$ (with CH_3)
DF-11	$[CH_3\,(CH_2)_3\,CH\,CH_2O]_2\,PSSZnSSP\,[OCH_2\,CH\,(CH_3)_2]_2$ (with C_2H_5)
—	$[((CH_3)_2\,CHCH_2O)_2\,PSS]_2\,Zn$

Additives DF-1, DF-2 and DF-12 were barium dialkyl dithiophosphates, and the remainder were zinc dialkyl dithiophosphates.

High-molecular-weight alcohols obtained by direct oxidation of a 330-390° paraffin fraction were used for the preparation of additives DF-1 and DF-5; alcohols obtained by oxidation of 270-330° paraffin fraction were used for the preparation of additive DF-2. The molecular weights of the alcohols corresponded to $C_{20}-C_{24}$ and $C_{16}-C_{20}$, respectively. Additive DF-8 was prepared from secondary octyl alcohol, 2-octanol, and additives DF-9 and DF-12 were prepared from a primary octyl alcohol, 2-ethyloctanol. Each of additives DF-10 and DF-11 were prepared from two alcohols, and, therefore, each contained radicals of different structure.

In the majority of experiments, paraffinic–naphthenic hydrocarbons separated by adsorption chromatography from a distillate oil from a sulfur-containing petroleum were subjected to oxidation. The amount of hydrocarbon oxidation was determined from the amount of oxygen absorbed by the hydrocarbons in a closed system.

All of the methal dialkyl dithiophosphates to some extent slowed down oxidation of the hydrocarbons, and thus are typical antioxidants. However, their activities as antioxidants were not equal, and the activity depended on the structure of the hydrocarbon radicals and the nature of the metal. The most active were the barium dialkyl dithiophosphates containing secondary hydrocarbon radicals.



The effect of additive DF-1 on the oxidation of paraffinic–naphthenic hydrocarbons. a) Paraffinic–naphthenic hydrocarbons; b) paraffinic–naphthenic hydrocarbons + 1% DF-1.

The figure presents the results of the oxidation of paraffinic–naphthenic hydrocarbons at different temperatures in the presence of additive DF-1 (a high-molecular-weight barium dialkyl dithiophosphate).

The dialkyl dithiophosphate antioxidants had their highest activity at temperatures up to 150°. The action of the antioxidants weakened at higher temperatures, apparently owing to thermal decomposition. The optimum concentrations of the various additives under the conditions used varied from 0.75 to 2.5%.

The oil from which the unstable paraffinic–naphthenic hydrocarbons were separated also contained monocyclic and bicyclic aromatic hydrocarbons and sulfur compounds. Certain aromatic hydrocarbons and, in particular, sulfur compounds in petroleum are natural antioxidants for the unstable hydrocarbons in petroleum. Therefore, the oil itself is highly stable. The natural inhibitors present in the oil render metal dialkyl dithiophosphate synthetic antioxidants ineffective; under these conditions, the synthetic antioxidants exert no appreciable effect on the oxidation of the oil.

Metals and their oxides (Fe, Cu, CuO) serve as catalysts for the oxidation of hydrocarbons. It has been shown that oils become unstable in the presence of metals in spite of the presence of natural inhibitors.

The catalytic effect of metals can be reduced or eliminated by the use of metal dialkyl dithiophosphates. Thus, for example, DF-1 additive increased the stability of oil in the presence of metals. Dialkyl dithiophosphates, which are surface-active substances, are apparently adsorbed on the metal surface, thereby exerting an indirect positive effect on the stability of the oil during oxidation by atmospheric oxygen.

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SYNTHESIS OF α-FURYLNITROETHYLENE AND INVESTIGATION OF ITS ABILITY TO UNDERGO POLYMERIZATION

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There has been extremely little investigation of the polymerization of nitrated heterocyclic monomers. In connection with an investigation of the possibility of preparing high-molecular-weight compounds of the heterocyclic series containing nitro groups in the polymer chain, we have prepared α-furylnitroethylene and tested its ability to undergo polymerization.

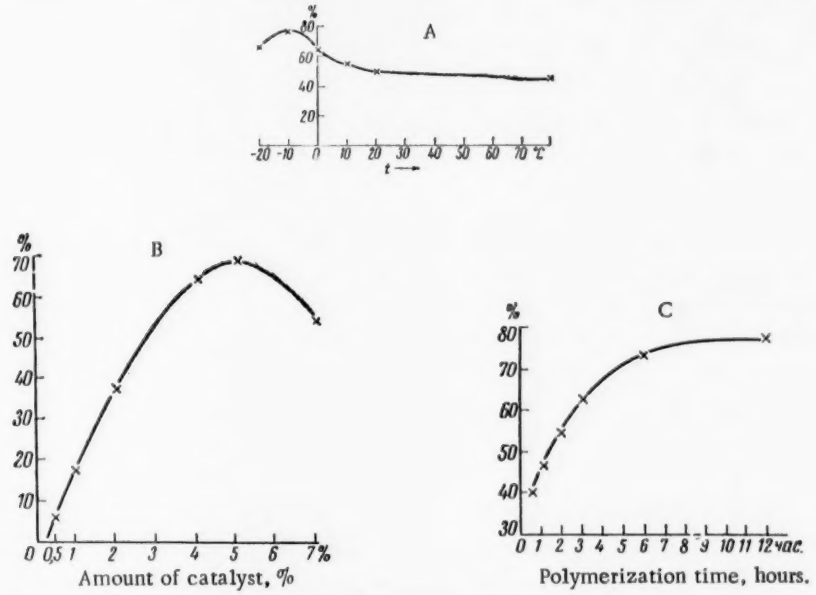
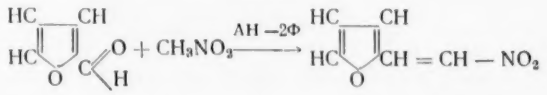


Fig. 1. Yield of α-furylnitroethylene polymer in the presence of sodium methylate catalyst as a function of temperature (A), amount of catalyst at optimum polymerization temperature, −10° (B), and polymerization time (C).

The literature describes three methods for the preparation of α-furylnitroethylene: 1) condensation of furfural and nitromethane in the presence of a base [1], 2) condensation of furfural and nitromethane in the presence of sodium methylate [2], and 3) the interaction of diketones with nitroparaffins [3].

Synthesis of the α-furylnitroethylene used in this work was carried out by condensing furfural with nitromethane in the presence of an anion-exchange resin. The yield was 38-46%.



The constants of this product differed little from those given in the literature. Three types of catalyst – anionic, cationic, and free-radical – were selected for the study of the polymerization of α-furylnitroethylene.

The polymerization of α-furylnitroethylene was investigated in the presence of boron trifluoride etherate, ammonium persulfate, and sodium methylate. No polymer was formed when boron trifluoride etherate was used as the catalyst.

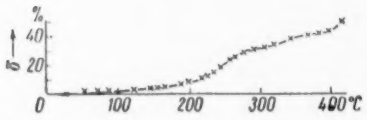


Fig. 2. Deformation–temperature curve for α-furylnitroethylene polymer prepared in the presence of sodium methylate catalyst; 100-g load.

Emulsion polymerization of α-furylnitroethylene in the presence of ammonium persulfate gave a polymer yield of only 6-8%; the polymer was an amorphous brown powder. It is evident that cationic and free-radical catalysts have practically no catalytic effect on the polymerization of α-furylnitroethylene.

Investigations of the polymerization of α-furlynitroethylene in the presence of sodium methylate showed that it is possible to obtain extensive polymerization in the presence of this catalyst.

We investigated the yield of polymer as a function of temperature, amount of catalyst, and reaction time (Fig. 1). The reaction was investigated at temperatures ranging from −20 to +80°, the amount of catalyst was varied from 0.5 to 7%, and the polymerization time was varied from 30 minutes to 12 hours.

As is apparent from the results presented in Fig. 1, the highest yield obtained from the polymerization of α-furylnitroethylene in the presence of sodium methylate, 74.5%, was obtained at a temperature of −10°, a reaction time of 6 to 7 hr, and a catalyst concentration of 5% (with respect to monomer). The polymer was thermally stable, infusible, and insoluble in the usual organic solvents.

Figure 2 shows a deformation–temperature curve for α-furylnitroethylene polymer prepared by polymerization under optimum conditions in the presence of sodium methylate catalyst. The curve was obtained at a load of 100 g.

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3. V. V. Perekalin and A. S. Sopova, Usp. khim. 24, No. 5, 613 (1955).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

GEM DIINDANDIONYLALKANES

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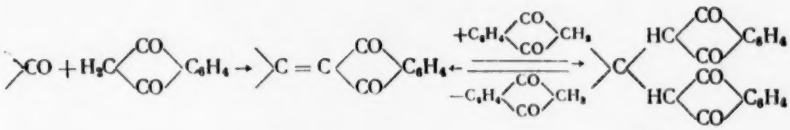
Translated from Doklady Akademii Nauk SSSR, Vol. 139, No. 3, pp. 597-600, July, 1961
Original article submitted April 1, 1961

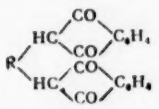
In a series of works (see [1] and the literature cited) we studied the condensation of indandione-1,3 with several quinones and aromatic aldehydes, and we showed that depending upon the reaction conditions and the quinone or aldehyde used there may be formed "ylidene" (A) as well as diindandionyl compounds (B) according to the general scheme



(A) (B)

This reaction has not been studied much in the case of aliphatic aldehydes. By condensing indandione-1,3 with formaldehyde, Radulescu [2] obtained methylene bis (indandione) or diindandionylmethane – a white crystalline substance melting at about 201°. With acetaldehyde in pyridine solution he obtained a finely crystalline, rose-colored substance melting at 227°, which he assumed to be diindandionylethane, but which he did not identify more definitely. Later, Ionescu [3] noted that diindandionylethane has a yellow color and melts at 254°, but he also did not investigate it further. Therefore the question arises, whether these writers obtained the same substance, and if not, which of them prepared diindandionylethane.

Gem Diindandionylalkanes



No.	Name	R	Melting point °C	Found, %		Calculated, %		Yield, %	Ultraviolet absorption curves	
				C	H	C	H		CHCl$_3$	NaOH
—	Diindandionylmethane	CH_2	201 (2)	—	—	—	—	—	—	—
I	DND*-ethane	CH_3CH	155	75,50	4,61	75,48	4,40	79,8	1	8
II	DND-propane	$CH_3 \cdot CH_2 \cdot CH$	140—142	75,98	4,88	76,08	4,94	58,1	2	9
III	DND-butane	$CH_3(CH_2)_2 \cdot CH$	115—117	76,30	5,17	76,30	5,20	73,0	3	10
IV	DND-isobutane	$(CH_3)_2 \cdot CH \cdot CH$	170—172	76,28	5,27	76,30	5,20	68,0	4	11
V	DND-pentane	$CH_3(CH_2)_3 \cdot CH$	92,5—94,5	76,75	5,50	76,67	5,55	50,0	5	12
VI	DND-isopentane	$(CH_3)_2 \cdot CH \cdot CH_2 \cdot CH$	120 CH_3OH	76,54	5,61	76,67	5,55	45,0	6	13
VII	DND-isohexane	$(HC_3)_2CH(CH_2)_3 \cdot CH$	63 dec.	77,03	5,84	77,00	5,88	58,60	7	14

* DND-diindandionyl.

It was Radulescu's [4] opinion that alkylidenebis(indandiones) can be prepared only up to ethylidenebis(indandione) because in the case of the higher aldehyde homologs self-condensation of indandione to form the anhydride

of bis(indandione) or biindone takes place faster than the condensation of indandione with the aldehyde. In fact, Ionescu [3] obtained only alkylideneindandionbiindones and alkylidenebis(biindones) when he condensed indandione with aliphatic aldehydes beginning with propionic aldehyde. He did not obtain diindandionylalkanes.

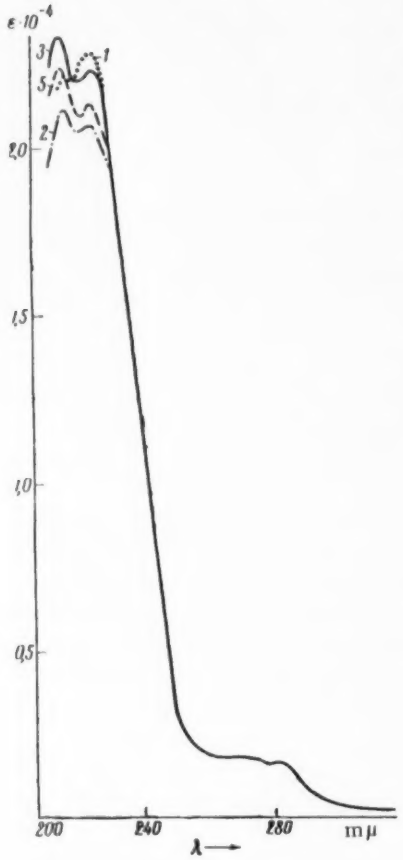


Fig. 1.

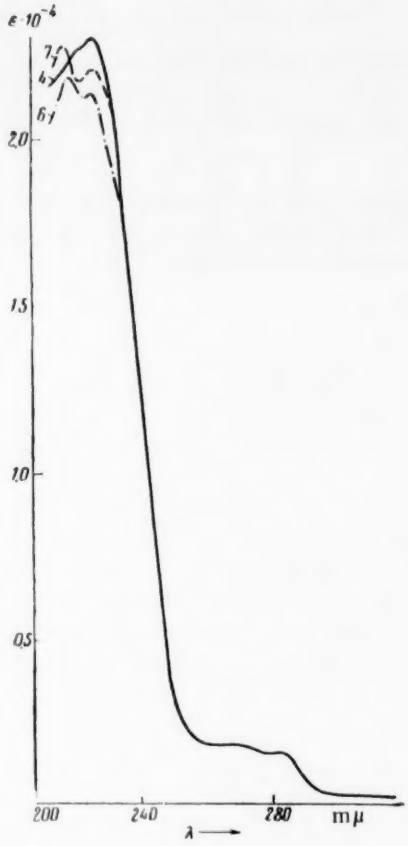


Fig. 2.

Because it had been established experimentally that diindandionyl compounds frequently split off readily a molecule of indandione (B → A) in a solution of alcohol or acetic acid, and that they are stable in an alkaline medium, we therefore condensed aliphatic aldehydes with indandione in an alkaline medium. In spite of the fact that in an alkaline medium aldehydes readily undergo an aldol condensation and also forms tars, the reaction may be directed towards a predominant formation of diindandionyl compounds under certain conditions (a low temperature, which slows up the self-condensation of indandione and conversion of aldehydes into tars, but which does not influence the condensation of indandione with aldehydes). In the condensation of aliphatic aldehydes which are only slightly soluble in water it was necessary to use mechanical stirring.

In this way we successfully condensed indandione with acetic, propionic, butyric, valeric, and caproic aldehydes. The salts of the respective diindandionylalkanes which were formed in this reaction were readily soluble in water. The free diindandionylalkanes were liberated by acidifying the solutions. A good yield was obtained of diindandionylethane (I) with m. p. 155°, which was different from the diindandionylethanes described by Radulescu and Ionescu. It is possible that they isolated an anhydride of diindandionylethane – the corresponding pyran.

The diindandionylalkanes (see Table 1) are white crystalline substances, very soluble in organic solvents. Their solubility increases as the aliphatic chain becomes longer. The diindandionylpentanes and diindandionylhexane were very soluble also in ether, which made their isolation and purification difficult. Light caused the diindandionylalkanes to turn yellow.

Because diindandionyl compounds have a characteristic absorption in the short-wave region of the ultraviolet spectrum [5] we confirmed the structures of the diindandionylalkanes (I-VII, the table) by recording their ultraviolet absorption spectra in a solution of chloroform (curves 1-7) and in alkali (curves 8-14), in Figs. 1-4. These curves are similar to the absorption curves of diindandionylarylmethanes [5], but in chloroform the more intense maximum of the diindandionylalkanes is split into two peaks: at 240 and 248 mμ ($\epsilon = 2.1 \cdot 10^4 - 2.3 \cdot 10^4$). The splitting of the characteristic maximum to a greater or less degree has also been observed in the case of other diindandionyl compounds [5]. In the region of 293-332 mμ there is a maximum of weak intensity ($\epsilon = \sim 0.2 \cdot 10^4$), but which is characteristic of diindandionyl compounds and their derivatives.

In an alkaline medium the nature of the absorption spectra of diindandionylalkanes (curves 8-14) agrees with that of the absorption spectra of the enolate forms of other diindandionyl compounds [5]. Here, as a result of the formation of another chromophoric system – α, β-unsaturated ketone – a small bathochromic shift occurs, and the intensity of the characteristic maximum is increased about two times ($\epsilon = 4 \cdot 10^4 - 5.5 \cdot 10^4$).

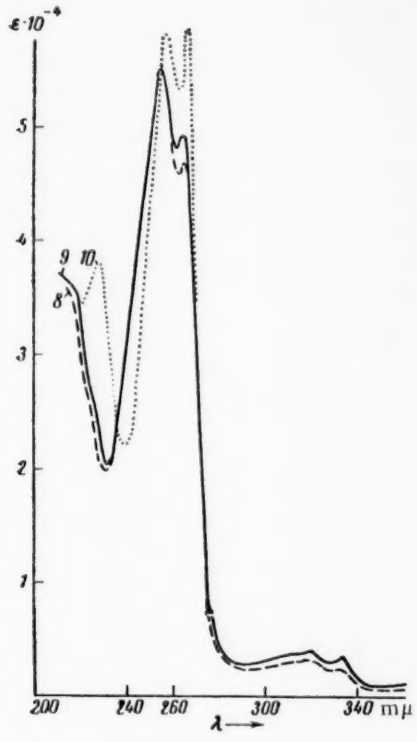


Fig. 3.

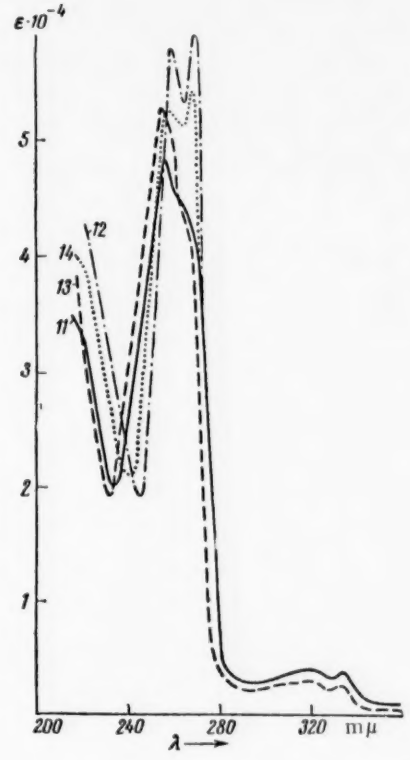


Fig. 4.

EXPERIMENTAL

Diindandionylalkanes (I-VII). Ten g (0.07 mole) of indandione-1,3 was dissolved in 100 ml of 5% KOH while cooling with ice, and to the cold solution was added 3-5 ml (0.035 mole) of a pure aliphatic aldehyde and the mixture was stirred for several hours. In the case of acetic and propionic aldehydes four hours' stirring was sufficient while 12 hours' stirring was necessary for valeric and caproic aldehydes. The dark-red solution was filtered, diluted to 500 ml with water, and added drop by drop while stirring to 200 ml of dilute HCl. A yellow precipitate formed. In the case of propionic and butyric aldehydes an oil may separate. It was dissolved in methanol, and crystals of the condensation product separated. When the precipitate contained biindone (the alkaline solution of the precipitate was a reddish-violet color) it was dissolved in 10% KOH and the potassium salt of biindone thus formed was filtered off. The diindandionylalkane salt remained in solution. The diindandionylalkane was liberated by acidifying the solution.

Each diindandionylalkane (I-IV) in the dry state was purified by treating it with ether, dissolving the residue in chloroform, and adding ether which precipitated white crystals of the diindandionylalkane. The diindandionylpentanes (V and VI) and diindandionylhexane (VII) were treated with CCl_4 because these compounds are quite soluble in ether. The residue from the CCl_4 treatment was crystallized from ether. The substance was precipitated from the ether filtrate with petroleum ether.

Condensation of acetic and propionic aldehydes with indandione took place readily without stirring when an alkaline solution of the two reactants was allowed to stand for 24 hr in a refrigerator.

Diindandionylalkanes dissolve readily in alkalis giving reddish-orange solutions, and in concentrated sulfuric acid – reddish-violet solutions.

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5. L. S. Geita and G. Ya. Vanag, Izv. AH Latv. SSR, No. 3 (152) 93 (1960).

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SPECTRAL MEASUREMENTS IN MIXED SOLVENTS BASED ON ALKANES AS A METHOD OF STUDYING THE INTERACTION OF SUBSTANCES WITH SOLVENTS

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(Presented by Academician B. A. Kazanskii, March 21, 1961)
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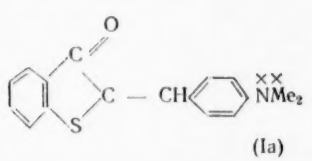
Original article submitted March 18, 1961

Investigations ([1-6] and others) have led to the conclusion that solvatochromic* spectral shifts are caused by two kinds of interactions of solutes with solvents: universal interaction (collective) and specific (individual) [6b]. There was no experimental method of determining which of these effects was the predominating one in a given case.

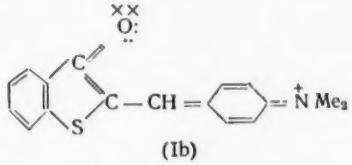
Absence of isosbestic points for spectra in pyridine, water, and their mixtures [7-9] also indicated that in solution under the influence of the medium gradual changes in mesostructure take place, "whereupon these changes can give an infinite number of intermediate shapes" [8]. The use of pyridine-water mixtures is quite unsuitable for solving the problem of the nature of the interaction of each of these solvents with the solute: 1) both solvents—pyridine and water – may exhibit not only universal but also specific interaction; 2) the picture may be complicated by the formation of a hydrate in the solution $[C_5H_5N...HOH] \rightleftharpoons [C_5H_5N]^+OH^-$ [11].

Spectra with a fine vibrational structure and which are the most similar to the absorption spectra of gases are obtained by dissolving substances in hexane. Alkanes are standard solvents exhibiting only universal interaction with a solute which is therefore in its simplest form. With these considerations in mind we began a spectroscopic study of solvatochromic changes of spectra in mixed solvents based on alkanes. Diluting with n-hexane the solutions of dyes in different solvents made it possible to trace the beginning of the solvatochromic effect in each individual case. Three types of spectral change have been observed up to the present time.

We used the method mentioned above for studying the solvatochromism of 2-(p-dimethylaminobenzylidene)-3-keto-2,3-dihydrothionaphthene (Ia) the mesostructure of which is the result of an electronic shift to the side of the structure (Ib): (Ia)⇝(Ib).**



(Ia)



(Ib)

First type of spectral change: gradual shifting of the curve. As the composition of a quinoline—hexane solvent mixture changes the shape of the spectral curve usually changes only on the left of the maximum. As the content (molecular percentage) of hexane in the mixture increases the curve shifts towards the short-wave region, and at the same time a secondary maximum gradually develops (Fig. 1). The same type of spectral change is observed with mixtures of benzene—hexane, chlorobenzene—hexane, and apparently other solvents the interaction of which with (I) is esentially of the universal type.

* The meaning of the term "solvatochromism" should be broadened to include the change in shape of a spectral curve, the positions and intensities of the maxima resulting from the influence of solvents, and at the same time not limited to the visible part of the spectrum (this has already been adopted in the case of the term "chromophore").

** The symbol ⇝ indicates a decrease in molecular energy due to conjugation (meso state) as compared with energy values calculated on the basis of possible limiting ("extreme") structural formulas [13].

Second type of spectral change: development of a new absorption band. The absorption maximum of compound (I) in alcohol (99.5%),(Fig. 2, curve a) is a new maximum, and not a displacement of the first or second maxima observed in hexane (Fig. 2, curve 6). Beginning with a certain composition of the solvent mixture alcohol–hexane (84 mole % alcohol and lower) all the spectral curves (Fig. 2, curves 1-6) intersect at one isosbestic point. This type of spectral change is also observed with solutions of (I) in mixtures of hexane with methanol or with acetic acid, i.e., with solvents which undergo a vigorous specific reaction with (I).

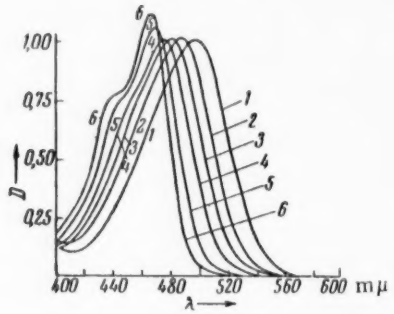


Fig. 1. Absorption spectra of solutions of (I) in quinoline–hexane mixtures of various compositions. 1) 100% quinoline; 2) 62.7 mole % quinoline; 3) 36.8 mole % quinoline; 4) 28.2 mole % quinoline; 5) 5.7 mole quinoline.

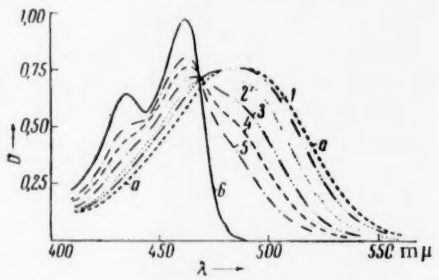
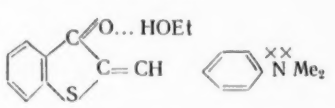


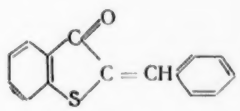
Fig. 2. Absorption spectra of solutions of (I) in alcohol–hexane mixtures of various compositions. a) 100% Alcohol; 1) 84 mole % alcohol; 2) 59.7 mole % alcohol; 3) 36 mole % alcohol; 4) 19.9 mole % alcohol; 5) 10.6 mole % alcohol; 6) 100% n-hexane.

The existence of an isosbestic point is usually considered to be indirect evidence of the presence in the solution of an equilibrium between two substances or between two forms of the same substance. We showed previously that (I) exists in two isomeric forms A and B [12]. However, the presence of an isosbestic point in Fig. 2 cannot be due to an equilibrium between the A and B forms of substance (I); 1) the isosbestic point of this equilibrium, which develops as a result of irradiation of the solution and which is almost undetectable in alcohol, lies at 512 mμ and shifts depending upon the composition of the solvent mixture; 2) we did all our experiments on solvatochromism in the dark with pure form A, whereas the transformation of form A into form B, according to our observations, takes place only in the presence of light.

Thus, we have some basis for assuming that the isosbestic point in Fig. 2 at 468 mμ corresponds to an equilibrium between an alcohol–dye solvate of a definite composition (for example, II) (in future we shall refer to this simply as "solvate") and the unsolvated dye.



(II)



(III)

On the assumption that curve 1 (Fig. 2) represents the spectrum of the solvate and that the spectrum of the unsolvated dye molecule is the same in the solvent mixture as in pure hexane (Fig. 2, curve 6), we attempted to find curves 2-5 (Fig. 2) by calculation. The following equations hold for each of these curves (we shall refer to curve 4 and the corresponding solution 4 by way of illustration):

$$C_s = (D_{490}/D^0_{490})\, C_{\text{total}} \tag{a}$$

$$C_n = C_{\text{total}} - C_s \quad \text{or} \quad C_n = C_{\text{total}} - D_{490}/D^0_{4(90)}\, C_{\text{total}} \tag{b}$$

$$D_{\text{total}} = \varepsilon_n\, C_n l + \varepsilon_s C_s l, \tag{c}$$

$$\varepsilon_n = D^0_n/(C_{\text{total}} l); \qquad \varepsilon_s = /D^0_s(C_{\text{total}} l), \tag{d}$$

where D_{490} – optical density from curve 4 at 490 mμ; D^0_{490} – optical density at 490 mμ from curve 1; C_{total} – overall (total) concentration of dye in solution; C_n – concentration of unsolvated dye in solution 4c, C_s – concentration of solvate in solution 4; Dtotal – optical density from curve 4; ϵ_n and ϵ_s – the molecular extinction coefficients of the unsolvated dye and solvate respectively; 1) thickness of the solution layer; D^0_n – optical density from curve 6; D^0_s – optical density from curve 1.

Comparison of Calculated* and Measured Optical Densities of Solutions of Substance (I) in a Mixed Solvent Composed of Different Proportions of Alcohol and Hexane

No.** of curve	Mole % alcohol in mixture	C^*_s	C^*_n	D^{***}_{total} 410 mμ		D_{total} 420 mμ		Dtotal 430 mμ		Dtotal 440 mμ		D_{total} 450 mμ		D_{total} 460 mμ	
				calc.	found	calc.	found	calc.	found	calc.	found	calc.	found	calc.	found
1	84	1	0	–	0.13	–	0.16	–	0.23	–	0.35	–	0.48	–	0.61
2	59.7	0.92	0.08	0.14	0.13	0.17	0.17	0.27	0.27	0.37	0.38	0.50	0.50	0.64	0.64
3	36	0.785	0.215	0.16	0.14	0.20	0.21	0.32	0.32	0.40	0.43	0.52	0.55	0.69	0.69
4	19.9	0.631	0.369	0.17	0.17	0.23	0.25	0.37	0.39	0.44	0.48	0.55	0.60	0.74	0.75
5	10.6	0.463	0.537	0.19	0.18	0.25	0.28	0.43	0.45	0.48	0.52	0.59	0.64	0.80	0.80
6	0	0	1	–	0.24	–	0.34	–	0.59	–	0.59	–	0.68	–	0.97

D_{total} 470 mμ		Dtotal 480 mμ		D_{total} 490 mμ		D_{total} 500 mμ		D_{total} 510 mμ		D_{total} 520 mμ		D_{total} 530 mμ		D_{total} 540 mμ	
calc.	found	calc.	found	calc.	found	calc.	found	calc.	found	calc.	found	calc.	found	calc.	found
–	0.72	–	0.76	–	0.76	–	0.69	–	0.53	–	0.34	–	0.18	–	0.09
0.71	0.72	0.70	0.72	–	0.69	0.64	0.59	0.49	0.41	0.31	0.23	0.17	0.10	0.08	0.05
0.69	0.71	0.61	0.65	–	0.58	0.54	0.44	0.41	0.26	0.26	0.13	0.14	0.06	0.07	0.02
0.65	0.70	0.50	0.56	–	0.46	0.43	0.30	0.33	0.16	0.21	0.07	0.12	0.02		
0.62	0.66	0.39	0.46	–	0.33	0.32	0.19	0.24	0.09	0.16	0.04	–	–		
–	0.539	–	0.071	–	0	–	0	–	0	–	0	–	0	–	0

* The initial assumptions and method of calculation are given in the text of this paper; C_s – concentration of solvate in the solution, calculated according to (a); C_n – concentration of dye not solvated with alcohol [calculated according to (b)].

** No. of curves as shown in Fig. 2.

*** Found from corresponding curve and calculated according to (e).

Equation (a) is accurate because the dye dissolved in pure hexane does not absorb light at 490 mμ. Equation (b) is based on the fact that the total dye concentration was constant for all solutions whose spectra are compared in Fig. 2. Equation (c) follows from the assumption that the solution contains only two types of absorbing particles: unsolvated dye molecules and a solvate of definite composition. Equation (d) follows from our initial assumption.

Equation (c) can be transposed into the form:

$$D = D^0_n\left(1 - (D_{490}/D^0_{490})\right) + D^0_s(D_{490}/D^0_{490});$$

Values of Dtotal, calculated by means of Eq. (e) and measured directly from curve 4 agree satisfactorily in the wavelength region of 410-480 mμ (see table). At wavelength greater than 490 mμ the calculated and measured values diverge considerably. Thus, the assumption that in a solution of substance (I) there is an equilibrium between a solvate (dye–alcohol) of definite composition and the unsolvated dye does not explain all the complications which are actually encountered.

Third type of spectral change: λ_{max} does not shift; the secondary maximum becomes the more intense maximum. We observed this form of spectral change with 2-benzylidene-3-keto-2,3-dihydrothionaphthene (III).

If we compare λ of the more intense maxima we find that the solvatochromic shift of the maximum in going from hexane to benzene amounts to 14 mμ (compare curves 6 and 1, Fig. 3). However, when the absorption spectra

were measured in the mixed solvents benzene–hexane (Fig. 3) or alcohol–hexane, it was found that the more intense maximum was transformed into a secondary maximum, while the secondary maximum developed and became the more intense. The real solvatochromic effect however consists not in the displacement of λ_{max}, but in a characteristic change in shape of the spectral curve.

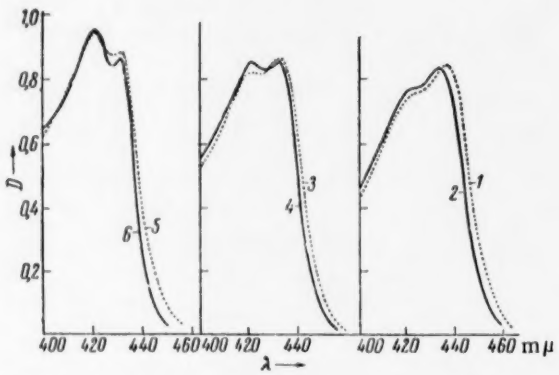


Fig. 3. Absorption spectra of solutions of (III) in benzene–hexane mixtures of various compositions. 1) 100% benzene; 2) 77.4 mole % benzene; 3) 59.5 mole % benzene; 4) 38.6 mole % benzene; 5) 14.1 mole % benzene; 6) 100% hexane.

In the case of mixed solvents based on alkanes, the spectroscopic method, as compared with other methods, makes it possible to differentiate more precisely and to classify the effects of solvents on the spectrum of a dissolved substance. It is hoped that in many cases this method will prove to be useful for observing the specific interaction of a solvent with a solute.

We are grateful to M. M. Shapkina for assistance in measuring the spectra.

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POLYMERIZATION OF ACETONITRILE AND OTHER NITRILES

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In the work reported in [1], using acetone as the monomer we were able to show that by the application of the principle of ordering the molecules of monomer in the reaction system, it is possible to carry out polymerization of monomers which, according to the laws of thermodynamics, cannot be converted to polymer directly from the liquid state. In the case of acetone, we were able to accomplish this by first freezing the monomer and then polymerizing it in the solid state. Freezing apparently leads to a change in the sign of the entropy of polymerization (the difference between the entropies of the initial and final states of the system) by decreasing the entropy of the initial state.

In the present work, this principle was applied with the aim of carrying out the polymerization of nitriles across the $C \equiv N$ bond. Polymerization of nitriles must be accompanied by the formation of one $C=N$ bond and one $C-N$ bond for each $C \equiv N$ bond. Neglecting, for the moment, the energy of conjugation, this process should take place with absorption of heat, approximately 11 kcal/mole (the energies of the $C \equiv N$, $C=N$ and $C-N$ bonds are, respectively, 149, about 84, and 53.5 kcal/mole [2]). The conjugation energy, which is liberated with the formation of the $-C=N-C=N-\ldots$, bond system, will make up the deficit in the most favorable case, making the heat of reaction close to 0. Since the conversion of liquid monomer to solid polymer is always accompanied by a decrease in entropy ($\Delta S < 0$), polymerization of nitriles across the $C \equiv N$ bond is impossible under ordinary conditions (taking the change in heat content as $\Delta H = -Q \cong 0$ and $\Delta S < 0$, the free energy change is $\Delta F = \Delta H - T\Delta S > 0$). We have been able to carry out the polymerization of a number of nitriles (acetonitrile, propionitrile, tolunitrile, benzonitrile, trifluoroacetonitrile, and others) by ordering the monomer molecules in solid complexes, which they form readily with coordination unsaturated metal halides ($ZnCl_2$, $BeCl_2$, $TiCl_4$, $AlCl_3$, $SnCl_4$, etc.). These complexes are crystalline substances of constant composition (usually, $MeX_n \cdot 2RCN$). The formation of such complexes from the starting materials is accompanied by a considerable decrease in the entropy of the system, which reaches 49 cal/deg·mole in the case of the complex $TiCl_4 \cdot 4Py$ [3], for example. There is some reason to suppose that the monomer molecules in such complexes are packed in a manner favorable to their combination in molecular chains [4]. When the metal halide-nitrile complexes were heated at temperatures of 180-350° in hermetically sealed vessels (sealed glass ampoules or autoclave) in the absence of atmospheric mositure and oxygen, polymerization of the ordered nitrile molecules took place with the formation of chains constructed of alternating carbon and nitrogen atoms:

$$\ldots -\underset{\displaystyle R}{\overset{\displaystyle |}{C}}=N-\underset{\displaystyle R}{\overset{\displaystyle |}{C}}=N-\underset{\displaystyle R}{\overset{\displaystyle |}{C}}=N-\ldots$$

In this process, the metal halide actually fills the role of an agent which permits the chemical equilibrium in the system monomer–polymer to be shifted toward the formation of polymer. At the conclusion of the reaction, the inorganic salt can be washed from the polymer with an appropriate solvent (water, ammonia, acids). Like attempts to polymerize nitriles at high pressures (of the order of 10,000 atm) [5], heating nitriles in which there has been dissolved only a small amount of one of the salts indicated above leads only to the formation of cyclic trimers.

Data obtained from i.r., spectroscopy were in accordance with the structural formula presented above for polynitriles. Figure 1 shows the i.r. spectrum of polyacetonitrile prepared by polymerization of acetonitrile complexed with $ZnCl_2$ ($2CH_3CN \cdot ZnCl_2$). The samples used in the i.r. investigation were prepared from powdered polymer by pressing it into tablets with KBr. The broad intense band in the region of 1580 cm^{-1} corresponds to absorption of a system of conjugated $C=N$ bonds. The absorption bands in the region of 1409 and 1352 cm^{-1} can be assigned to symmetrical deformation vibrations of the CH_3 groups. The absorption in the region of 1138 cm^{-1} can possibly be assigned to wagging vibrations of the methyl group.

In all probability, the polymerization process proceeds by a stepwise mechanism. The molecular weight of the polymer increases with polymerization time. Yellow, low-molecular-weight, water-soluble products are formed first, and with an increase in polymerization time the color of the polymer gradually changes from yellow to dark brown and black. Thus, the polyacetonitrile obtained by heating a complex of acetonitrile and $ZnCl_2$ at 250° for 5 hr was a dark brown powder soluble in dimethylformamide. With an increase in heating time, the polymers formed were soluble only in concentrated acids (formic, phosphoric, sulfuric). An increase in the polymerization time at 250° to 10 hr and longer resulted in the formation of black insoluble polymers.

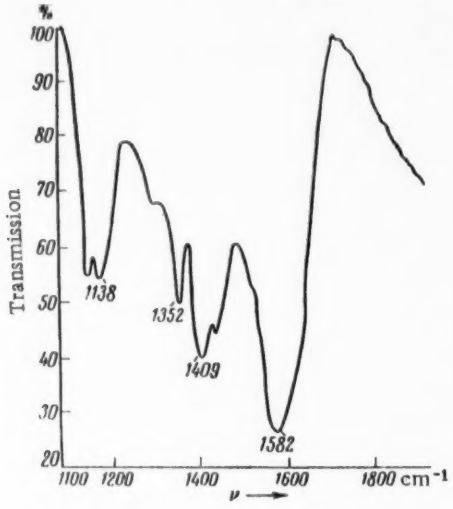

Fig. 1. I. r. spectrum of polyacetonitrile.

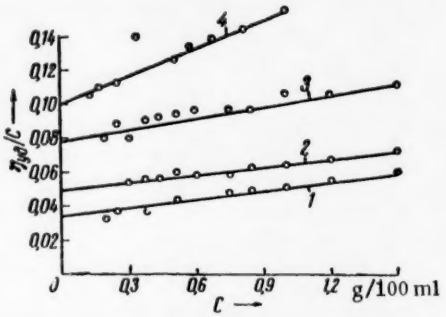

Fig. 2. Concentration dependence of the specific viscosity of solutions of samples of polyacetonitrile prepared under different conditions. Polymerization temperature, 250°; polymerization times: 1) 4 hr; 2) 5 hr; 3) 6 hr; 4) 7 hr.

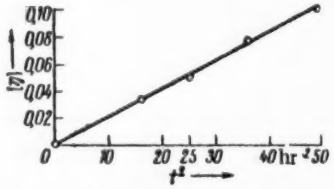

Fig. 3. Dependence of the intrinsic viscosity of polyacetonitrile on the square of the polymerization time; polymerization temperature, 250°.

Polymerization conditions	σ_{20°, ohm^{-1} × cm^{-1}	σ_0, ohm^{-1} × cm^{-1}	E, ev
250°, 5 hr	$1{,}7\cdot10^{-11}$	$3{,}0\cdot10^{-5}$	0,35
250°, 6 hr	$1{,}9\cdot10^{-9}$	$7{,}3\cdot10^{-4}$	0,30
250°, 8 hr	$3{,}2\cdot10^{-8}$	$2{,}4\cdot10^{-3}$	0,28
300°, 8 hr	$1{,}9\cdot10^{-6}$	$7{,}7\cdot10^{-2}$	0,25
350°, 8 hr	$1{,}0\cdot10^{-5}$	$6{,}8\cdot10^{-2}$	0,21

Figure 2 shows the results of measurements of the viscosity of sulfuric acid solutions of samples of polyacetonitrile prepared at different polymerization times. The intrinsic viscosity increased with an increase in polymerization time up to the point where the polymers were converted to insoluble compounds. Similar relationships were observed with an increase in reaction temperature. Thus, at 300°, a black insoluble polymer was formed just 5 hr after the beginning of polymerization. If it is assumed that each polymer chain in the complex grows by a stepwise mechanism independently of other, previously formed molecular chains, then the change in the degree of polymerization (P) with time (t) can be described by the equation

$$\frac{dP}{dt} = k \quad \text{or} \quad P = kt,$$

where k, to a first approximation, can be assumed to be a constant which depends on temperature and the structure of the complex. Intrinsic viscosity is related to the degree of polymerization by the well-known relationship $[\eta] = KP^{\alpha}$. For very stiff polymers such as the polynitriles, α is probably close to 2. Therefore

$$[\eta] \cong k^2Kt^2 = Kt^2.$$

Figure 3 shows that the experimental dependence of $[\eta]$ on t^2 can indeed be described by a straight line which extrapolates through the origin.

The polynitriles are highly stable thermally; they possess semiconductor properties, and their e.p.r. spectra are characteristic of polyconjugated systems. Over wide limits, the electrical conductivity changes with a change in polymerization temperature, and the variation is readily reproducible. The results of measurements of the electrical conductivity of samples of polyacetonitriles prepared under different conditions showed that the conductivity increases with an increase in polymerization time and temperature. The electrical conductivity at room temperature increased by six orders of magnitude with a change in the polymerization temperature from 250 to 350° and in polymerization time from 5 to 8 hr. The temperature dependence of the electrical conductivity of all samples over the temperature interval of 20 to 200° strictly obeyed the equation $\sigma = \sigma_0 e^{-E/RT}$. The energy of activation of the electrical conductivity decreased with an increase in polymerization time and temperature, varying for the samples investigated within the limits of 0.35 to 0.2 ev (table). The decrease in the activation energy was accompanied by an increase in the preexponential constant, which indicates the absence of a "compensation effect."

Thus, the present work has shown that through the application of the principle of preliminary ordering of the monomer molecules, one more multiple bond, the C≡N bond, has been added to the list of bonds capable of entering into polymerization reactions. This opens up the possibility of using the various nitriles to prepare a new class of polymers with conjugated bonds in the main chain.

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THIN-LAYER CHROMATOGRAPHY OF CEREBROSIDES

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The separation, purification, and characterization of cerebrosides still remain a difficult problem. In addition to the classical fractionation methods used for this purpose, chromatographic methods have recently attracted attention; thus cerebrosides have been separated from other sphingolipides by means of an aluminum oxide column [1] and by passage through a mixture of Florisil and ion exchange resins [2]. Weiss [3], using silica gel chromatography with gradient elution with a mixture of chloroform and methanol, was able thereby to separate the individual kerasin and cerebron together with a substance which was not a cerebroside but which had a closely similar structure, though the structure has not been conclusively established as yet.

The weakest point in all investigations of the separation of cerebrosides and, to a considerable extent, other sphingolipides is the absence of precise methods for control of the fractionation, which frequently completely devaluates the separation methods. The use for this purpose of paper [4, 5] and impregnation [6] chromatography did not yield the desired result, a fact which can be confirmed by our data. In all cases, owing to the closely similar and highly hydrophobic natures of the individual cerebrosides, these substances give one diffuse spot with an R_f exceeding 0.85-0.90.

We have established that thin-layer chromatography, which has not previously been used for this purpose, is a completely suitable method of control of the separation of cerebrosides. Just at the completion of the present investigation there appeared a paper by Jatzketitz and Mehl [7] in which data were presented on silica gel thin-layer chromatography of various lipides, including two which were identified as cerebrosides (kerasin and cerebron).

We have carried out thin-layer chromatography of the cerebroside fraction of sphingolipides from beef cattle brain; this fraction was preliminarily freed from sphingomyelins, sulfatides, and gangliosides by passage of a pyridine solution through a basic aluminum oxide column (Brockmann activity of II) [1]; the cerebroside fraction contained no phosphorus or sulfur. The plates used in the chromatography were prepared as follows: a homogeneous paste consisting of 6.7 g of KSK silica gel (150-200 mesh), 0.35 g of calcined gypsum, and 19 ml of water was applied to a carefully purified plate (13 × 18). The plate was dried for 2-3 hr in air and 2 hr at 105°. The plates were stored in a desiccator over calcined calcium chloride. In contrast to the mobile phase of the authors cited above [7], our mobile phase was an anhydrous system. The most suitable system proved to be a mixture of chloroform and methanol containing 10 to 20% methanol.

The mixture of cerebrosides, 40 γ in 20 microliters of a 2:1 mixture of chloroform and methanol, was placed at a distance of 1.5 cm from the edge of the plate, which was then placed in a cell containing the solvent and left for 1 hr; during this time the solvent front usually rose 10-12 cm. After being dried in air, the chromatogram was sprayed with concentrated sulfuric acid. The plate was heated for 10-15 minutes under a lamp, and the cerebrosides developed as black spots. The cerebroside fraction used in the preliminary experiments, purified as indicated above, gave four spots with the chloroform–methanol system (80:20): to strong spots with R_f of 0.41 and 0.51 and two weak spots with R_f of 0.75 and 0.85.

This method was then used for control of a preparative separation of cerebrosides by partition chromatography in a silica gel column. As mentioned above, Weiss [3] was able to isolate by this method only kerasin and cerebron from sphingolipides, and the individuality of these compounds remains unclear, since the author did not use any chromatographic control to determine whether they were individual compounds. Weiss used only a small amount of lipides in the separation (70-200 mg), citing the requirement of starting with not more than a calculated 4 mg of lipides per gram of silica gel. We showed that a quite sharp separation can be obtained with a charge of 8 mg of cerebroside

fraction per gram of silica gel. However, in place of the gradient elution used by Weiss (which was not sufficiently effective, since the properties of the individual cerebrosides are closely similar), we carried out the elution considerably more slowly than did Weiss; the rate was 40-45 ml/hr.

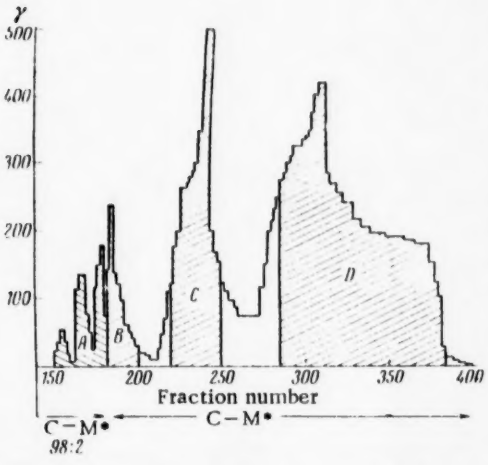

Fig. 1. Chromatographic separation of 400 mg of a mixture of cerebrosides in a silica gel column (in γ of galactose).

We carried out a chromatographic separation of 400 mg of a cerebroside fraction (containing no phosphorus or sulfur, and containing 21.3% galactose, 21.7% galactose calculated for cerebron). The separation was carried out in a 20 × 400 mm column containing 50 g of silica gel (KSK, 75-100 mesh). The cerebrosides were dissolved in 42 ml of chloroform–methanol mixture (20:1) was introduced into the column, which had been given a preliminary flushing with a chloroform–methanol mixture (2:1) and pure chloroform. Elution was carried out with the following solvents (in order): 230 ml of chloroform, 720 ml of a mixture of chloroform and methanol (98:2), and 1150 ml of a second mixture of chloroform and methanol (95:5). The rate of elution was 10-11 ml per hour, and the eluate was collected in 5.5 ml fractions in a collector. An 0.5 ml sample was removed from each fraction, and the content of galactose was determined by the anthrone method as modified by Roe [8]. The elution curve of the cerebrosides showing the content of galactose in the individual fractions is shown in Fig. 1. The fractions obtained during elution of the column were combined in four groups, A, B, C, and D, as shown in Fig. 1. Thin-layer chromatography of all four groups of cerebrosides (80:20 chloroform–methanol solvent) showed that groups B, C, and D, which were characterized by well-formed circular spots, contained individual cerebrosides. Group A gave two spots, of which one corresponded in R_f value to the substance of group B, while the other was not sufficiently sharp. A second thin-layer chromatographing of all groups of fractions in a less polar chloroform–methanol system (85:15) gave better results, which revealed the presence of five clearly outlined separate spots in group A (Fig. 2a) and confirmed the individuality of the cerebrosides of groups B, C, and D (Fig. 2b). The R_f values obtained by thin-layer chromatography of groups A, B, C, and D in both solvents are shown in the table.

Fraction No.	Group	Rf in chloroform–methanol system		Fraction No.	Group	Rf in chloroform–methanol system	
		80 : 20	85 : 15			80 : 20	85 : 15
150—182	A	0,70	0,50	183—200	B	0,70	0,50
		0,75—0,85	0,56	200—250	C	0,60	0,21
		—	0,62	285—385	D	0,55	0,16
		—	0,68				
		—	0,74				

This result, obtained through the use of thin-layer chromatography, is of considerable interest despite its preliminary nature. Up to the present, the existence of four individual cerebrosides has been definitely established: cerebron (phrenosin), kerasin, nervon, and hydroxynervon; the latter still has not been separated in a pure form. Moreover, in the earlier literature there are indications of the separation from the hydrolyzates of cerebroside, fractions of fatty acids which are not component parts of the compositions of the four cerebrosides enumerated above [9, 10]; there has been a tendency to consider these acids to be the result of hydrolysis of traces of other sphingolipides in the insufficiently purified cerebroside fractions. Moreover, the existence of glucocerebrosides, in addition to galactocerebrosides, is well known. These have been separated from the spleen [11], and have not as yet been detected in brain tissue [11, 12].

• C–M = chloroform–methanol.

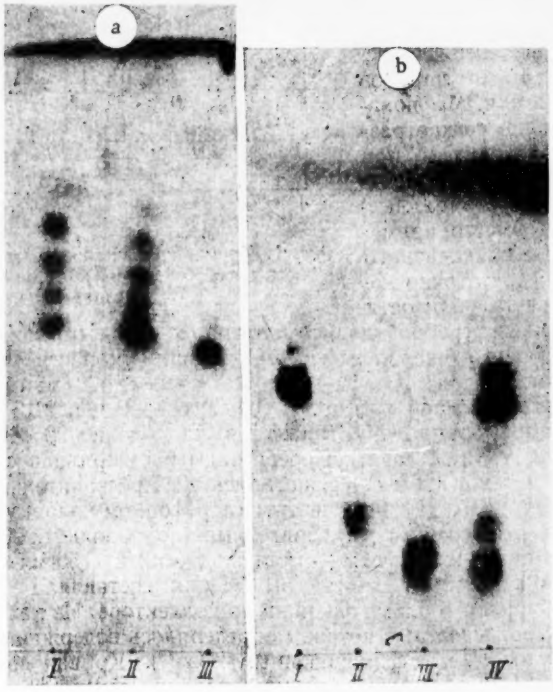

Fig. 2. Silica gel thin-layer chromatography of cerebrosides in chloroform–methanol (85:15). a: I) 10 γ of cerebrosides of group A (R_f = 0.50, 0.56, 0.62, and 0.74); II) mixture of 10 γ of cerebrosides of group A and 10 γ of cerebroside of group B; III) 10 γ of cerebroside of group B (R_f = 0.50); b: I) 20 γ of cerebroside of group B (R_f = 0.50); II) 10 γ of cerebroside of group C (R_f = 0.21); III) 20 γ of cerebroside of group D (R_f = 0.16); IV) 40 γ of a mixture of cerebrosides before separation in the silica gel column.

When it is remembered that, in contrast to earlier investigators, we started with a cerebroside fraction which had been carefully purified from traces of other sphingolipides by chromatography, it seems unlikely that the components of group A are noncerebroside impurities. The chromatographic analysis of the fractions of group A should rather be considered as a quite definite indication of the presence of previously unknown cerebrosides in our cerebroside fraction of beef cattle brain; these are distinguished primarily by their fatty acids. Our data suggest that the cerebrosides of groups B, C, and D are kerasin, hydroxynervon, and cerebron. Naturally, a more definite conclusion as to the nature of the components of groups A, B, C, and D can be made only after a study of their hydrolysis, a study which we are currently carrying out.

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THE HOMOLOGOUS SERIES OF URANIUM OXIDES, U_nO_{2n+2}

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(Presented by Academician A. P. Vinogradov, February 6, 1961)
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The development of inorganic chemistry over the past five to seven years has been characterized by the discovery of homologous regularities in the chemical composition of the series of oxides of each of the transition elements. Interesting regularities of this type had previously been known only in organic chemistry. The discovery of such series in inorganic chemistry was first made by the Swedish crystallochemist Magneli and co-workers during studies of the oxides of tungsten, molybdenum, vanadium, and titanium [1-8].

Thus, it was found that tungsten and molybdenum oxides correspond to the homologous formulas M_nO_{3n-1} and M_nO_{3n-2}, and the oxides of titanium and vanadium correspond to the formula M_nO_{2n-1} (where M is the metal and n is an integer). For example, all of the titanium oxides of the homologous series Ti_nO_{2n-1} from n = 1 to n = 10, i.e., the oxides TiO, Ti_2O_3, Ti_3O_5, Ti_4O_7, Ti_5O_9, Ti_6O_{11}, Ti_7O_{13}, Ti_8O_{15}, Ti_9O_{17}, and $Ti_{10}O_{19}$, were synthesized, separated as chemical individuals, and characterized by x-ray methods.

Many investigators in foreign countries have been occupied by the study of the chemistry of uranium oxides (see [10]). The chemistry of the uranium–oxygen system is extremely complex owing to the formation of oxides of variable composition as well as the so-called "nonstoichiometric" oxides, i.e., oxides which do not correspond to a simple stoichiometric ratio of uranium to oxygen, for example, U_3O_7, U_3O_8, U_4O_9, U_5O_{12}, etc.

On the basis of the assumption of the dual chemical nature of uranium [9], according to which uranium acts more like the lanthanides or more like the elements of groups IV A, V A, and VI A depending on its valence, it may be assumed that the compositions of the uranium oxides will also correspond to some general homologous regularity. Indeed, this assumption is apparently confirmed by all available data on the composition and structure of uranium oxides, as will be shown below.

In Fig. 1, the vertical lines along the UO_x axis denote the compositions of uranium oxides corresponding to the general formula U_nO_{2n+2} (where n in an integer). The figure shows that all of the first eight homologs of this series actually exist as oxides which have been established in the experimental investigations cited below. In the figure, these oxides are indicated by the corresponding formulas over the composition ordinates.

n = 1. UO_4^{2-}. Uranium tetraoxide has not been isolated in the free state, but it exists in the form of the uranate ion U_4^{2-}, and also in the form of hydrates, for example, the well-known dihydrate $UO_4 \cdot 2H_2O$ [10].

n = 2. $U_2O_6 = UO_3$. Uranium trioxide is the usual form of the highest oxidation state of uranium; it has long been solidly established by the investigations of numerous authors. At least five polymorphic modifications of UO_3 are known [11].

We recently confirmed the finding of Zachariasen [12] as to the structure of the hexagonal oxide, α-UO_3, which was prepared in our laboratory by L. M. Kuznetsov by thermal decomposition of uranium oxalate trihydrate, $U(C_2O_4)_2 \cdot 3H_2O$. In precisely the same manner we confirmed, by neutron diffraction, a cubic structure of the ReO_3 type for δ-UO_3; this was first found by E. Wait [13]. Moreover, we synthesized two other oxides having the composition UO_3, but the structures of these have still not been determined.

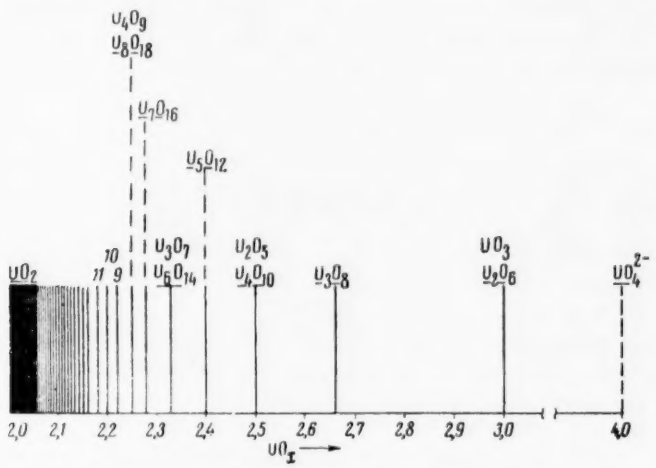
n = 3. U_3O_8. The oxide most frequently encountered in chemistry is the so-called uranoso-uranic oxide, which is known in two polymorphic modifications. The low-temperature modification of U_3O_8 is stable up to about 400° and has a rhombic structure with the lattice constants a = 11.91; b = 6.71; c = 8.27 kX; it is also encountered as two monoclinically distorted modifications with the same parameters and angles of 89 and 91°, respectively [14]. Above 400°,

U_3O_8 has a trigonal structure with the lattice constants a = 6.801 and c = 4.128 kX [15]. It is possible that both U_3O_8 modifications are oxides of variable composition with an oxygen deficiency. In spite of many attempts in this direction, the location of the atoms in the two modifications cannot be considered to be definitely established.

n = 4. $U_4O_{10} = U_2O_5$. This oxide has been found in many investigations, and most recently Rundle, Baenziger, Wilson and McDonald [16] have regarded it as the low-oxygen limit of a homogeneous region possibly extending from $UO_{2.5}$ to UO_3. According to other data [17], this region extends from $UO_{2.56}$ to $UO_{2.66}$ (U_3O_8). In view of the fact that the equilibrium diagram of the uranium–oxygen system has not yet been established, the precise temperature and concentration limits of the stability of the oxide U_2O_5, like those of the other uranium oxides, are still not known. The most reliable crystallochemical data on U_2O_5 have been reported by Rundle and co-workers [16], who were able to prepare a single crystal of this oxide and to establish that the unit cell is orthorhombic with the dimensions a = 8.27; b = 31.65; c = 6.72 A; the locations of the atoms have not been determined.

n = 5. U_5O_{12}. During studies of the products of the low-temperature oxidation of uranium dioxide, Gronvold and Haraldsen [17] and also Perio [18] found a tetragonal oxide having a composition close to $UO_{2.40}$, which corresponds to the formula U_5O_{12}. According to Perio, the lattice constants are a = 5.364 and c = 5.531 A, and c/a = 1.031. Locations of the atoms have not been established.

n = 6. $U_6O_{14} = U_3O_7$. The first indication of the existence of this oxide was found by P. Jolibois [19]. Subsequently, during studies of the low-temperature oxidation of uranium dioxide, the existence of the oxide $UO_{2.33}$ = $= U_3O_7$ was confirmed by a number of investigators [17, 18, 20]. This oxide has a tetragonal structure, and, according to Perio [18], a = 5.436 and c = 5.389 A, and c/a = 0.991. J. S. Anderson gives for another crystalline modification c/a = 1.016. The locations of the atoms in U_3O_7 have not been established.



The homologous series of uranium oxides U_nO_{2n+2}.

n = 7. U_7O_{16}. This compound is apparently a third tetragonal uranium oxide with an axis ratio of c/a = 1.010; it was discovered by Perio [18] along with the two preceding oxides ($UO_{2.40}$ and $UO_{2.33}$). Its theoretical composition $UO_{2.285} = U_7O_{16}$ is in good agreement with the experimental region $UO_{2.28-2.31}$ proposed by Perio [18], which he was unable to define more accurately.

n = 8. $U_8O_{18} = U_4O_9$. The existence of this oxide has been firmly established by numerous investigations, of which we may cite the recent work of Hoekstra and Siegel [21], Hering and Perio [22], and Belboch, Piekarski and Perio [23]. Until recently, it has been assumed that $U_4O_9 = UO_{2.25}$ corresponds to the upper oxygen-saturation limit of a phase of variable composition in cubic uranium dioxide, $UO_{2.00-2.25}$ [10]. Moreover, numerous x-ray powder investigations have shown that with an increase in the degree of oxidation there is a continuous decrease in the lattice constant for the cubic lattice from a = 5.47 A for UO_2 to a = 5.43 A for $UO_{2.25}$ (approximate values).

However, Perio [23] was recently able to synthesize a U_4O_9 single crystal. X-ray investigation of this crystal confirmed the cubic structure, but it also gave an unexpectedly large value, four-fold along the edge, of the lattice

constant a = 4 · 5.433 = 21.73 A. This fact indicates the discreteness of the chemical composition of the oxide U_4O_9. The locations of the atoms cannot be considered to be definitely established.

Certain considerations limit further advancement toward greater values of n in the homologous series U_nO_{2n+2}. Analysis of this formula together with consideration of the figure shows that an increase in n rapidly leads to a disappearingly small difference in the chemical compositions of neighboring oxides, owing to which an investigator first finds progress difficult and then impossible in an experimental regard; the "forest" of the infinite multitude of discrete uranium oxides tend to the composition UO_2 but never quite reach it exactly.

These considerations apparently explain the well-known fact that in practice the experimenter never has an oxide of the ideal composition UO_2, but always has a somewhat more oxidized sample UO_x, where x is slightly more than two, for example, $UO_{2.008}$ or $UO_{2.010}$ [18].

It is, nevertheless, possible to hope that such oxides as U_9O_{20}, $U_{10}O_{22} = U_5O_{11}$, $U_{11}O_{24}$, and others will soon be established experimentally.

The poor knowledge of the details of crystal structure make it impossible at the present time to connect the homology of the chemical composition of uranium oxides with the location of the atoms in the oxides. Undoubtedly, such a connection must exist, and the powers of crystallochemists should be directed toward the discovery of this connection and to a search for "molecules" of the composition U_nO_{2n+2}, without which the chemical nature of the homology cannot be clear in the present case.

We may also remark that the establishment of the homology of the composition of inorganic compounds opens up a completely new route for interpreting the chemical nature of the Berthollides, which are similar to the variable composition oxides $UO_{2.0-2.25}$. In view of the existence of homologous series, the similar Berthollides cannot be considered as either "a phase of variable composition" or as a "continuous set of compounds," as has been done until recently. The new data force a change in these views, and it is necessary to consider a region of compositions such as $UO_{2.2-2.25}$, as a discontinuous, discrete set of distinct chemical individuals united by a general homologous regularity and having very similar chemical compositions, crystal structures, and properties.

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INVESTIGATION OF THE THERMODYNAMIC PROPERTIES OF CERIUM–LEAD, PRASEODYMIUM–LEAD, AND NEODYMIUM–LEAD ALLOYS

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The thermodynamic properties of alloys containing rare earth elements have received but little study up to the present time. The equilibrium diagrams of the systems Ce–Pb and Pr–Pb have been determined, but not with sufficient accuracy, and the diagram of the system Nd–Pb has not been determined [1]. It is assumed that all of the above equilibrium diagrams are of the same type as the equilibrium diagram of the system La–Pb. The existence in this system of the compounds $LaPb_3$, LaPb, and La_2Pb has been established. Heterogeneous regions exist within the concentration limits (in atom fractions of Pb) of from 0.97 to 0.75, 0.75 to 0.50, 0.50 to 0.33, and 0.33 to about 0.005.

TABLE 1. Activities of Lead

Atom fraction Pb	Alloy	a_i		Atom fraction Pb	Alloy	a_i	
		T = 993° K	T = 1073° K			T = 993° K	T = 1073° K
1,0		1,0	1,0	0,50–0,33	Ce — Pb	0,0063	0,0123
0,97–0,75	Ce — Pb	0,776	0,794		Nd — Pb	0,0199	0,0316
	Nd — Pb	0,776	0,794		Pr — Pb	0,0133	0,0219
	Pr — Pb	0,776	0,794	0,33–0,005	Ce — Pb	0,0003	0,0014
0,75–0,50	Ce — Pb	0,524	0,661		Nd — Pb	0,0008	0,0036
	Nd — Pb	0,417	0,525		Pr — Pb	0,00005	0,0002
	Pr — Pb	0,205	0,302				

TABLE 2. Partial Thermodynamic Functions for the Interval 993-1073°K

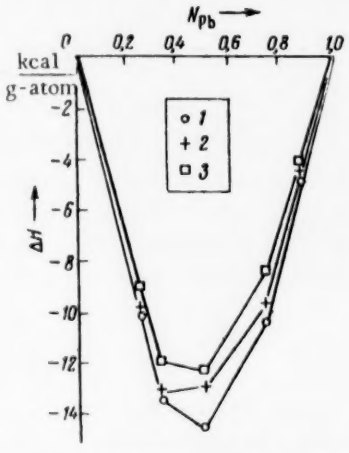
Atom fraction Pb	Alloy	$\Delta \bar{H}_{Pb}$, kcal/g-atom	$\Delta \bar{S}_{Pb}$, kcal/degree/g-atom	Atom fraction Pb	Alloy	$\Delta \bar{H}_{Pb}$, kcal/g-atom	$\Delta \bar{S}_{Pb}$, kcal/degree/g-atom
1,0		0	0				
0,97–0,50	Ce — Pb	—0,6	—0,1	0,50–0,33	Ce — Pb	—17,8	—7,8
	Nd — Pb	—0,6	—0,1		Nd — Pb	—12,3	—4,5
	Pr — Pb	—0,6	—0,1		Pr — Pb	—12,8	—4,3
0,75–0,50	Ce — Pb	—6,1	—4,8	0,33–0,005	Ce — Pb	—40,8	—24,9
	Nd — Pb	—6,1	—4,4		Nd — Pb	—39,9	—25,9
	Pr — Pb	—4,9	—2,1		Pr — Pb	—36,7	—17,4

We have been able to determine the activities of lead in its alloys with cerium, praseodymium, and neodymium by measuring the pressure of the saturated vapor. Alloys with lead concentrations corresponding to the above

heterogeneous regions were investigated. Three or four alloys were studied in each region. The apparatus and method have been described in [2]. Rare earth elements having a purity of 99.9% and spectroscopically pure lead were used in the preparation of the alloys.

TABLE 3. Integral Thermodynamic Functions for the Interval 993-1073°K

Atom fraction Pb	Alloy	ΔH kcal/g-atom	ΔS cal/deg-g-atom
0.75	Ce–Pb	−10.4	−6.7
	Nd–Pb	−9.8	−6.0
	Pr–Pb	−8.7	−3.8
0.50	Ce–Pb	−14.6	−8.2
	Nd–Pb	−13.0	−7.6
	Pr–Pb	−12.4	−5.4
0.33	Ce–Pb	−13.6	−8.3
	Nd–Pb	−13.3	−8.6
	Pr–Pb	−12.1	−5.7



Integral heats of formation of the alloys Ce–Pb (1), Nd–Pb (2), and Pr–Pb (3).

The activity, a_i, of one of the components of the alloy may be determined from the vapor pressure measurement, and the chemical potential may then be calculated by means of the equation:

$$\Delta\mu_i = RT \ln a_i.$$

Measurements of the rate of evaporation of lead from the alloys (the rate of evaporation is proportional to the vapor pressure) were carried out over the temperature range of 700 to 900°; the activity of the lead in the alloys was calculated for 720-800°. The data are presented in Table 1.

The partial molal heats and entropies of formation of the alloys were then calculated by well-known equations, and the intergral heats and entropies of formation of the alloys were calculated by graphical integration of the Duhem–Margules equation. Values of the partial molal thermodynamic functions of the lead are presented in Table 2.

It may be remarked that the integral heats of formation differed insignificantly among the three systems (Fig. 1). This indicates that the interactions of these rare earth elements with lead are all of the same type. The negative value of the entropy of formation is associated with the negative heat of formation, i.e., with a strengthening of the bond between the atoms in the alloy.

The error in the determination of the activity of lead was 1%, and the errors in the calculations of the heats and entropies of formation of the alloys were 20% and 25%, respectively.

Our data confirm the existence of three intermetallic compounds in the system Nd–Pb, the existence of the compound CePb, and the existence of the heterogeneous regions in conformity with the equilibrium diagram of the system La–Pb.

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INVESTIGATIONS IN THE FIELD OF MULTICOMPONENT NICKEL SYSTEMS

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Investigations of the interactions of metals in multicomponent systems are hampered by the difficulty of geometrically representing the complex equilibria and the structural diagrams of these systems.

Methods based on the projection of the sections used for constructing structural diagrams of multicomponent systems find only limited use in studies of real metallic systems. The method having the greatest prospects is the projection method proposed by V. P. Radishchev [1] and F. M. Perel'man [2], who developed the method toward selection of the optimum projection. The correct simple figures, simplexes, serve to represent the compositions of metallic systems: a triangle for a ternary system, a tetrahedron for a quaternary system, a pentatope for a quinary system, a hexatope for a senary system, a heptatope for a septenary system, etc.

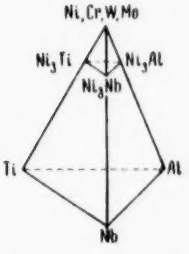

Fig. 1. One section of the seven-component system Ni–Cr–W–Mo–Nb–Ti–Al at 1100°.

It is possible to section a simplex, which yields a figure of one less dimension. Thus, for example, by sectioning a heptatope (representing a seven-component system) three successive times one may obtain a tetrahedron (representing a four-component system). The sectioning can be carried out so that one vertex of the tetrahedron will represent the composition of four components in a definite proportion (in conformity with the three sections).

Figure 1 shows one of the sections of the seven component system Ni–Cr–W–Mo–Nb–Ti–Al. The vertex of the resulting tetrahedron represents the composition of four components: Ni, Cr, W, Mo (in a specific proportion).

Since in the present investigation we were not interested in all of the general compositions of alloys possible for any ratios in the system Ni–Cr–W–Mo–Nb–Ti–Al, but only in those alloys which are multicomponent nickel solid solutions or adjoining phases, one additional sectioning of the tetrahedron was carried out through the compounds Ni_3Nb, Ni_3Ti, and Ni_3Al, as shown in Fig. 1.

Consequently, in studying nickel-rich alloys in the seven-component system Ni–Cr–W–Mo–Nb–Ti–Al, we were limited to a study of the quasi-quaternary system composed of a four-component nickel solid solution (provisionally denoted as γ_4), Ni_3Ti, Ni_3Al, and Ni_3Nb (in place of the large number of two-, three-, and four-, five-, and six-component systems present in this complex seven-component system).

In this investigation, we assumed that both the metallic compounds (Ni_3Ti, Ni_3Nb, and Ni_3Al) and the nickel solid solution (γ_4) remained unchanged during the course of the investigation.

On the basis that a solid solution represents a single phase in the equilibrium state [3, 4], it is possible to consider a binary, ternary, or more complex solid solution based on a given metal or metallic compound (with a specific ratio of the original metals) as one component.

In a number of cases, this makes it possible to reduce the study of multicomponent systems to an investigation of the equilibria among a multicomponent solid solution and one, two, or three elements or their chemical compounds, as we have shown for the study of the partial structural diagram of the five-component system Ni–Cr–W–Ti–Al [5] and one section of the eight-component system Ni–Cr–W–Mo–Nb–Ti–Al–C which was represented as a quasi-binary system of a six-component nickel solid solution (γ_6) and TiC [6].

The aim of the present investigation was to establish the region of distribution of the nickel solid solution in the quasi-quaternary system γ_4-Ni_3Ti–Ni_3Al–Ni_3Nb and to establish the phase composition in regions adjoining this solid solution.

The methods chiefly used in the investigation were microstructural analysis, x-ray structural analysis, and intermetallide and analysis.

The alloys investigated were fused in an arc furnace in an atmosphere of argon or in suspension under an atmosphere of helium in a furnace constructed for use without a crucible. In the preparation of the alloys, the metallic compounds Ni_3Al, Ni_3Nb, and Ni_3Ti (of precisely stoichiometric composition) and γ_4 (of precisely the composition of the four-component solid solution) were preliminarily fused in the arc furnace, and this material was then used as charge material. It was first established by microstructural and x-ray structural methods (see Figs. 2, 1-4), that after fusion and the appropriate heat treatment (1100° for 400 hr, cooled in air), the metallic compounds and the nickel solid solution (γ_4) were single-phase materials.

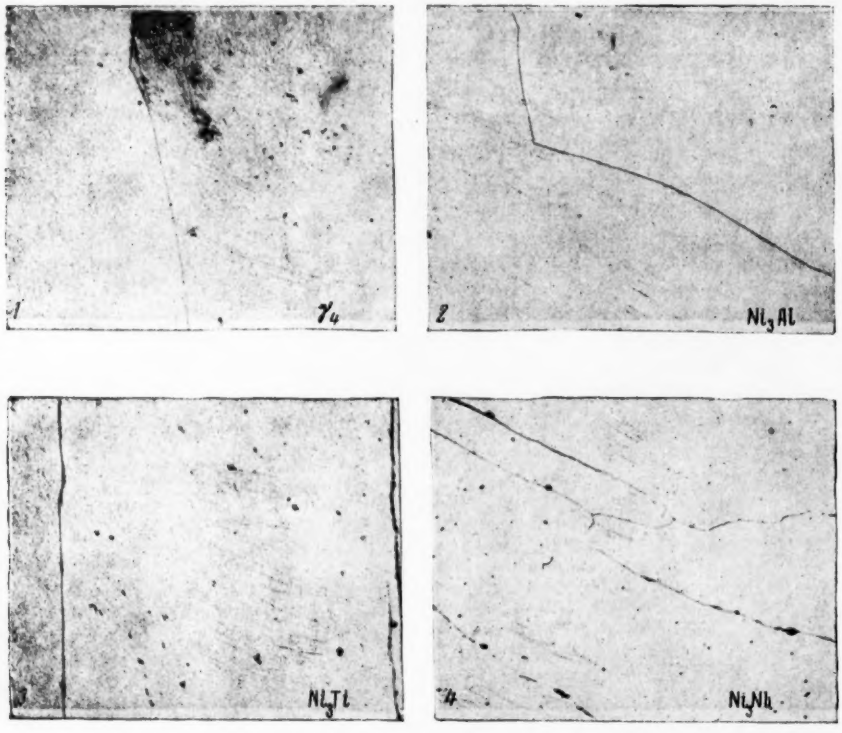

Fig. 2. Microstructures of the alloys after heat treatment (1100° for 400 hr, cooled in air): 1) four-component nickel solid solution (γ_4); 2) Ni_3Al metallic compound; 3) Ni_3Ti; 4) Ni_3Nb.

On the basis of our investigation and the literature data, schematic phase diagrams (for 1100°) were constructed for the four quasi-quaternary systems, which are the four sides of the tetrahedron under investigation: 1) γ_4-Ni_3Ti–Ni_3Al, 2) γ_4-Ni_3Al – Ni_3Nb, 3) γ_4-Ni_3Ti – Ni_3Nb, and 4) Ni_3Ti – Ni_3Al – Ni_3Nb.

The investigations showed that in the six-component alloys of the quasi-ternary systems indicated above there are single-phase, two-phase, and three-phase equilibria. No more than three phases were established in these alloys in the solid state. In order to confirm the data on the phase composition of the alloys obtained by microstructural analysis, x-ray structural* and intermetallide** analyses were carried out on individual alloys. The intermetallide and x-ray structural analysis results confirmed, in the main, the results obtained in the microstructural investigations.

* The x-ray structural analysis was carried out by S. A. Yuganova and co-workers in the Central Scientific Research Institute of Transport Mechanical Engineering.

** The intermetallide analysis was carried out by R. B. Golubtsova in the Institute of Metallurgy of the Academy of Sciences USSR and by L. A. Nudé in the Central Scientific Research Institute of Transport Mechanical Engineering.

Figure 3 shows a projection of the tetrahedron of the quasi-quaternary system γ_4-Ni_3Ti–Ni_3Al–Ni_3Nb on one of the coordinate planes; the three lateral faces of the tetrahedron with a common vertex corresponding to the γ_4-solid solution are readily apparent. Also readily apparent in Fig. 3 are the phase diagrams of the three quasi-ternary systems investigated in this work; the numbers in the circles indicate alloys on which intermetallide analysis was carried out. Three alloys from the region of the γ-nickel solid solution were investigated (Nos. 1, 3, and 4). The composition of No. 1 corresponded precisely to the composition of γ_4. Three alloys from the single-phase region of the γ-phase were also investigated (Nos. 13 and 17 and the compound Ni_3Al).

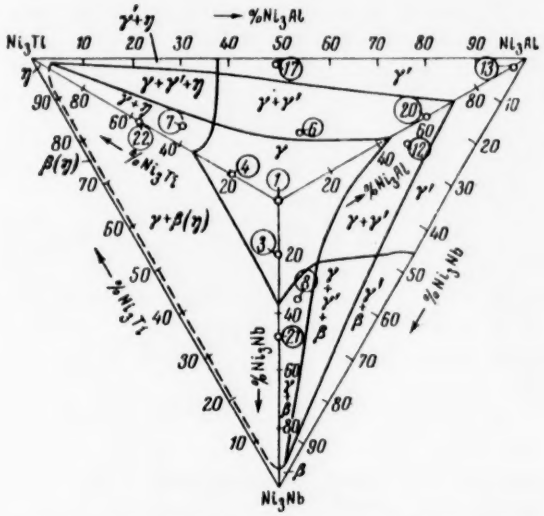

Fig. 3. Projection of the tetrahedron of the quasi-quaternary system γ_4-Ni_3Ti–Ni_3Al–Ni_3Nb. Point 1 (γ_4): Ni 81.0, Cr 10.0, W 6.0, Mo 3.0 wt.%.

Anodic solution of each of these alloys yielded no residue. This confirms that the alloys indicated are single-phase solid solutions. X-ray structural investigation also confirmed that alloys Nos. 13 and 17 are solid solutions based on the compound Ni_3Al.

The following alloys from the two-phase regions of the diagram were subjected to intermetallide analsis: from the region $\gamma + \gamma'$, alloys Nos. 6, 12, and 20; from the region $\gamma + \beta$, alloys Nos. 8 and 21; from the region $\gamma + \eta$, alloys Nos. 7 and 22.

Anodic solution of each of these alloys yielded a residue, which was present in their second phase. On the basis of microchemical and x-ray structural analyses of the residues separated from alloys Nos. 6, 12, and 20, there was present a γ'-phase solid solution based on the compound Ni_3Al and having a face centered cubic lattice.

Since the compositions of alloys Nos. 6, 12, and 20 were not the same, the amount of dissolved metals (Cr, W, Mo, Nb, and Ti) in the γ'-phase separated from these alloys differed. The lattice parameter of the γ'-phase changed with a change in composition.

Chemical and x-ray structural analyses of the residues separated from alloys Nos. 8 and 21 established that the η-phase is a solid solution based on the compound Ni_3Nb and has a rhombic structure [7]. The lattice parameters of the β-phase, which was separated from alloys Nos. 8 and 21, differed somewhat. This may be explained by the small difference in the chemical compositions of the phases separated and by the different locations of these alloys on the structural diagram (see Fig. 3).

Anodic solution of alloys Nos. 7 and 21 yielded residues which, on analysis, were found to consist of η-Ni_3Ti and to have a close packed hexagonal structure.

Microchemical analysis of the β-phase established that in addition to Ni and Ti, it also contained small amounts of Cr, W, Mo, and Al; this proved the presence of a solid solution based on Ni_3Ti. Apparently, during the formation of an Ni_3Ti phase in complex alloys, a solid solution based on this compound can be formed, although this compound does not have a region of homogeneity in the Ni–Ti binary system [8]. Alloys from the three-phase region of the diagram have been prepared and are being investigated, but these investigations have not yet been completed.

The following conclusions may be formed on the basis of this investigation. By carrying out several successive sections of multicomponent systems it is possible to study the partial structural diagrams of these systems. The components of these systems may be not only the individual elements, but also their solid solutions as well as metallic compounds. The ability of metals to form solid solutions and also the possibility of forming solid solutions between metallic compounds and between metals and metallic compounds leads to a decrease in the total number of solid phases present at equilibrium in multicomponent systems. It was established that there are not more than three phases in six-component alloys of the system Ni–Cr–W–Mo–Nb–Ti–Al. Microstructural, x-ray structural, and intermetallide analyses established the chemical compositions of the phases present at equilibrium (in the solid state) in certain six-component alloys of the system.

The types of crystal lattices of these phases and the lattice parameters were determined. The formation, in multicomponent alloys, not only of solid solutions based on the compound Ni_3Al, but also of solid solutions based on the compounds Ni_3Nb and Ni_3Ti was shown to be possible.

Since, in the majority of cases, alloys with special properties (for new fields of technology) are either solid solutions based on some metal or metallic compound or are heterophase materials (in which the solid solutions are additionally strengthened owing to finely dispersed separate metallide phases), the study of structural diagrams of multicomponent systems can be reduced to a study of the partial diagrams, individual sections of these diagrams, as we have shown by our study of nickel systems.

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A NEW METHOD FOR THE SYNTHESIS OF TRICHLOROMETHYL ORGANOMERCURY COMPOUNDS

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Several methods based on the use of carbenes – short-lived divalent carbon compounds – are known for the synthesis of organomercury compounds.

Thus, for example, methylene, generated from diazomethane, has been introduced between mercury and halogen with the formation of halomethyl organomercury compounds [1, 2]. Diphenylcarbene, generated from diphenyldiazomethane, reacts similarly [1]. Carbenes apparently are also involved in the synthesis of organomercury compounds by the reaction of hydrazones, aldehydes, and ketones with mercuric acetate [3, 4].

We found [5] that dichlorocarbene, formed by the action of potassium tert-butylate on chloroform, can also be introduced between mercury and chlorine with the formation of trichloromethyl organomercury compounds.* The present article describes a method based on this reaction, for the synthesis of trichloromethyl organomercury compounds:

$$R-Hg-Cl + :CCl_2 \rightarrow R-Hg-CCl_3.$$

Dichlorocarbene was reacted with mercuric chloride (R = Cl), phenylmercury chloride, p-nitrophenylmercury chloride, p-methoxyphenylmercury chloride, p-dimethylaminophenylmercury chloride, β-naphthylmercury chloride, trans-β-chlorovinylmercury chloride, and cis-β-chlorovinylmercury chloride.

The yields and certain properties of the trichloromethyl organomercury compounds prepared are reported in the table.

Starting material	Product	Yield, %	M.p., °C	Analysis	
				Found	Calculated
$HgCl_2$	CCl_3HgCl	2	178–180	Hg 56,83	Hg 56,60
C_6H_5HgCl	$C_6H_5HgCCl_3$	52	114–116	—	—
p-$O_2NC_6H_4HgCl$	p-$O_2NC_6H_4HgCCl_3$	31	141–143	C 19,23; 19,22; H 1,16; 1,20 Hg 45,74; 45,34	C 19,06 H 0,91 Hg 45,48
p-$CH_3OC_6H_4HgCl$	p-$CH_3OC_6H_4HgCCl_3$	85	123–123,5	C 22,87; 23,09; H 1,97; 2,02 Hg 47,30; 47,03	C 22,55 H 1,66 Hg 47,08
p-$(CH_3)_2NC_6H_4HgCl$	p-$(CH_3)_2NC_6H_4HgCCl_3$	49	117,5–118	Hg 45,60	Hg 45,66
β-$C_{10}H_7HgCl$	β-$C_{10}H_7HgCCl_3$	57	147–149	C 30,42; 30,32; H 1,93; 1,88; Hg 45,13	C 29,61 H 1,58 Hg 44,97
trans-ClCH=CHHgCl	trans-ClCH=CHHg—CCl_3	56	79–80	Hg 53,06	Hg 52,72
cis-ClCH=CH—HgCl	cis-ClCH=CH—Hg—CCl_3	10	Oil	—	—

*See also the recently published short communication by G. A. Razuvaev [6] on the synthesis of CCl_3HgCl and $C_6H_5HgCCl_3$ by the reaction of mercuric chloride and phenylmercury chloride with the sodium salt of trichloroacetic acid.

The presence of the CCl_3 group in the products was demonstrated by decomposition of the compound with hydrochloric acid and subsequent color reaction of the resulting chloroform.*

Acetylene was evolved when cis- and trans-β-chlorovinyltrichloromethylmercury was heated; both substances gave CCl_3HgBr when reacted with bromine:

$$ClCH = CH - Hg - CCl_3 \xrightarrow{Br_2} CCl_3HgBr + [ClCH = CHBr]^{**}.$$

Trichloromethylmercury chloride was formed by the action of chlorine on trans-β-chlorovinyltrichloromethylmercury:

$$\text{транс-}ClCH = CH - Hg - CCl_3 \xrightarrow{Cl_2} CCl_3HgCl + [ClCH = CHCl]^{**}.$$

Phenyltrichloromethylmercury was converted by the action of bromine to phenylmercury bromide:

$$C_6H_5HgCCl_3 \xrightarrow{Br_2} C_6H_5HgBr + [CCl_3Br]^{**}.$$

All of the compounds of the general formula $R-Hg-CCl_3$, where R is an aromatic radical, decomposed in accordance with the following scheme when heated in alcohol:

$$2R - Hg - CCl_3 \rightarrow 2R - Hg - Cl + [CCl_2 = CCl_2]^{**}.$$

Dibromocarbene, formed by the action of potassium tert-butylate on bromoform, could also be inserted between mercury and halogen. Thus, phenylmercury bromide gave phenyltribromomethylmercury in 41% yield. The latter melted at 98-99° (with decomposition).

$$C_6H_5HgBr + :CBr_2 \rightarrow C_6H_5HgCBr_3.$$

The reaction by which dihalocarbenes are introduced between metal and halogen is apparently rather general; it was found to be applicable to compounds of antimony, copper, cobalt, and certain other metals.

EXPERIMENTAL

Preparation of trichloromethylmercury chloride, CCl_3HgCl. To a suspension of 15 g (0.055 mole) of mercuric chloride in 90 ml of absolute benzene was added 8 ml (0.1 mole) of absolute chloroform; the reaction mixture was then stirred and cooled with water, and 4 g (0.1 g-atom) of dry potassium tert-butylate was added. The reaction mixture was stirred for 30 minutes after the addition of the butylate, and was then poured into water. The benzene layer was separated and dried, and the benzene was evaporated. The residue was washed with petroleum ether. The yield of trichloromethylmercury chloride was 0.4 g (2% of theoretical). The m. p. was 178-180° (from alcohol). The literature reports an m. p. of 173° [7].

Found %: Hg 56.83. Calculated %: Hg 56.60.

Preparation of phenyltrichloromethylmercury, $C_6H_5HgCCl_3$. To a suspension of 4.9 g (0.016 mole) of phenylmercury chloride in 100 ml of absolute benzene was added 5 ml (0.062 mole) of absolute chloroform and, gradually and with stirring, potassium tert-butylate prepared from 1.2 g (0.03 g-atom) of potassium; the reaction mixture was cooled with ice water during the addition of the potassium butylate. After a 30 minute stirring, the darkened reaction mixture was poured into water, and the precipitate was filtered and washed with benzene. Evaporation of the benzene left 1.7 g of $C_6H_5HgCCl_3$, m. p. 114° (from alcohol). The literature reports an m. p. of 114-116° [8]. The The benzene-insoluble residue was extracted with hot acetone, and a mixture of phenylmercury chloride and phenyltrichloromethylmercury (2.32 g) was obtained by evaporation of the acetone. Upon washing the mixture with benzene there was obtained 1.55 g of $C_6H_5HgCCl_3$ with an m. p. of 112-114°. The residue contained 0.55 g of unreacted phenylmercury chloride with an m. p. of 256°. The literature reports an m. p. of 258° [9]. The total yield of phenyltrichloromethylmercury was 3.25 g (52% of theoretical).

Heating the phenyltrichloromethylmercury in alcohol gave a quantitative yield of phenylmercury chloride with an m. p. of 255-256°. The literature reports an m. p. of 258° [9]. The action of a solution of bromine in carbon tetrachloride on a benzene solution of phenyltrichloromethylmercury gave a quantitative yield of C_6H_5HgBr with an m. p. of 270-271°. The literature reports an m. p. of 275° [10].

* A raspberry color appeared when the chloroform was heated with 10% NaOH and pyridine.

** The substance enclosed in brackets was not identified.

Preparation of p-nitrophenyltrichloromethylmercury, p-$O_2NC_6H_4HgCCl_3$. To a suspension of 5.2 g (0.012 mole) of p-nitrophenylmercury chloride in 35 ml of absolute dioxane was added 2.5 ml (0.031 mole) of absolute chloroform and, gradually and with stirring, 3.3 g (0.03 mole) of potassium tert-butylate; the reaction mixture was cooled with ice water during the addition of the potassium butylate. The reaction mixture was stirred for 30 minutes at room temperature after the addition of the potassium butylate. The precipitate was removed by filtration, a large part of the dioxane was distilled unter the vacuum of a water aspirator, and the organomercury compound was precipitated with water. The weight was 1.8 g. The dioxane-insoluble precipitate was washed with water and dried. The weight was 2.7 g. The combined precipitates were extracted with ether, and 1.22 g (31% of theoretical) of p-nitrophenyltrichloromethylmercury was obtained; it decomposed at 141-143°.

Found %: C 19.23, 19.22; H 1.16, 1.20; Hg 45.74, 45.34. Calculated %: C 19.06; H 0.91; Hg 45.48.

The residue contained 2.5 g of unreacted p-nitrophenylmercury chloride.

Preparation of p-methoxyphenyltrichloromethylmercury, p-$CH_3OC_6H_4HgCCl_3$. To a suspension of 4.2 g (0.012 mole) of p-anisylmercury chloride in 35 ml of absolute dioxane was added 3 ml (0.037 mole) of absolute chloroform and, gradually and with stirring, 2.8 g (0.025 mole) of potassium tert-butylate; the reaction mixture was cooled with ice water during the addition of the potassium butylate. The mixture was stirred for 30 minutes, and the precipitate was separated by filtration. The dioxane was distilled under aspirator vacuum, and the organomercury compound was precipitated with water. The precipitate was separated by filtration, washed with water, dried, and dissolved in cold benzene. The solution was filtered, and the benzene was evaporated. There was obtained 3.9 g (85% of theoretical) of p-$CH_3OC_6H_4HgCCl_3$. After two recrystallizations, the first from ether and the second from alcohol, the product melted at 123-123.5°.

Found %: C 22.87, 23.09; H 1.97, 2.02; Hg 47.30, 47.02. Calculated %: C 22.55; H 1.66; Hg 47.08.

When p-methoxyphenyltrichloromethylmercury was heated in alcohol, p-anisylmercury chloride was obtained in quantitative yield; m. p. 235-236°. The literature reports 239° [11].

Preparation of p-dimethylaminophenyltrichloromethylmercury, p-$(CH_3)_2NC_6H_4HgCCl_3$. To a suspension of 3.9 g (0.011 mole) of p-dimethylaminophenylmercury chloride in 40 ml of absolute benzene was added 2 ml (0.025 mole) of absolute chloroform and, gradually and with stirring, 2.5 g (0.022 mole) of potassium tert-butylate; the reaction mixture was cooled with ice water during the addition of the potassium butylate. The reaction mixture was stirred for 20 minutes after addition of the butylate was complete, and the precipitate was separated by filtration and washed with benzene. Evaporation of the benzene gave 2.3 g (49% of theoretical) and p-$(CH_3)_2NC_6H_4HgCCl_3$. After two recrystallizations from a mixture of benzene and alcohol, the product melted at 117.5-118°.

Found %: Hg 45.60. Calculated %: Hg 45.66.

The substance decomposed during storage.

Preparation of β-naphthyltrichloromethylmercury, β-$C_{10}H_7HgCCl_3$. To a suspension of 4 g (0.011 mole) of β-naphthylmercury chloride in 55 ml of absolute dioxane was added 2 ml (0.025 mole) of absolute chloroform and, gradually and with stirring, 2.5 g (0.022 mole) of potassium tert-butylate; the reaction mixture was cooled with ice water during the addition of the potassium butylate. The reaction mixture was stirred for 1 hr after completion of the addition of the butylate. The precipitate was separated by filtration, and a large part of the dioxane was distilled. The product was precipitated with water. The precipitated organomercury compound was separated by filtration, dried, and dissolved in benzene. The solution was filtered, and the benzene was evaporated. There was obtained 2.35 g of β-$C_{10}H_7HgCCl_3$ with an m. p. of 148-149°. The dioxane-insoluble precipitate was washed with water, dried, and extracted with acetone. Evaporation of the acetone gave a mixture of β-naphthylmercury chloride and β-naphthyltrichloromethylmercury, from which 0.45 g of β-$C_{10}H_7HgCCl_3$, m. p. 147-149°, was washed with cold benzene. The total yield of β-$C_{10}H_7HgCCl_3$ was 2.8 g (57% of theoretical).

Found %: C 30.42, 30.32; H 1.93, 1.88; Hg 45.13. Calculated %: C 29.61; H 1.58; Hg 44.97.

A total of 0.5 g of unreacted β-naphthylmercury chloride with an m. p. of 268° was recovered. The literature reports 270° [9].

Preparation of trans-β-chlorovinyltrichloromethylmercury, $ClCH = CH - HgCCl_3$. To a solution of 13.5 g (0.045 mole) of trans-β-chlorovinylmercury chloride in 90 ml of absolute benzene was added 8 ml (0.1 mole) of absolute chloroform and, gradually and with stirring, potassium tert-butylate prepared from 4 g (0.1 g-atom) of

potassium; the reaction mixture was cooled with ice during the addition of the potassium butylate. The reaction mixture darkened considerably. After addition of the potassium butylate was complete, the reaction mixture was poured into water. The solution was filtered from the black precipitate, and the benzene layer was separated and dried and the benzene evaporated. There was obtained 9.1 g (53% of theoretical) of trans-ClCH = CHHgCCl$_3$ with an m. p. of 79-80° (from alcohol).

Found %: Hg 53.06. Calculated %: Hg 52.72.

Thermal decomposition of the compound gave acetylene, which was identified by the formation of a red precipitate of copper acetylide. A solution of bromine in carbon tetrachloride was added to a benzene solution of trans-β-chlorovinyltrichloromethylmercury. A precipitate of trichloromethylmercury bromide, m. p. 160-162°, formed immediately. The literature reports an m. p. of 165° [7]. Pyridine was added to a solution of the bromide in benzene, the mixture was evaporated to 1 ml, and water was then added. The pyridine–trichloromethylmercury bromide complex was extracted with ether. Evaporation of the ether gave a yellow powder with an m. p. of 85.5-86.5° (from benzene). The literature reports an m. p. of 87° [7]. To a benzene solution of trans-β-chlorovinyltrichloromethylmercury was added a solution of chlorine in carbon tetrachloride. The resulting precipitate of trichloromethylmercury chloride was separated by filtration, washed with a small amount of hot water, dried, and recrystallized from benzene. It darkened at 176° and melted at 180°. The literature reports an m. p. of 173° [7].

Preparation of cis-β-chlorovinyltrichloromethylmercury, ClCH = CH – HgCCl$_3$. To a solution of 3.75 g (0.013 mole) of cis-β-chlorovinylmercury chloride in 40 ml of absolute benzene was added 3 ml (0.037 mole) of absolute chloroform and, gradually and with stirring, 2.85 g (0.025 mole) of potassium tert-butylate; the reaction mixture was cooled with ice water during the addition of the potassium butylate. The mixture was stirred for 30 minutes. The precipitate was separated by filtration and washed with benzene, and the benzene solution was evaporated. Part of the material decomposed. The blackened residue was extracted with benzene, and the benzene was rapidly evaporated. The oily residue was ground with petroleum ether. The petroleum ether-insoluble powder (0.82 g) melted at 75-77°. It did not give a color reaction for chloroform, and was unreacted cis-β-chlorovinylmercury chloride. The literature reports an m. p. of 78-79° [12]. Evaporation of the petroleum ether gave 0.5 g of cis-ClCH = CH – HgCCl$_3$ (10.5% of theoretical) in the form of an oil with a sharp odor. The addition of a solution of bromine in carbon tetrachloride to a benzene solution of the product resulted in precipitation of trichloromethylmercury bromide with an m. p. of 160-163°. The literature reports 165° [7].

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CHEMISORPTION OF ISOPROPYL ALCOHOL ON METAL OXIDE-γ-ALUMINA CATALYSTS

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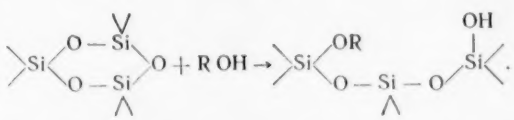
Direct measurements of chemisorption are almost always of interest, not only from the point of view of obtaining a detailed description of sorption phenomena and clarification of the role of chemical forces in adsorption, but also in connection with questions of catalysis, since more or less stable chemical bonds are formed during the formation of the activated complex between molecules of the reacting substance and atoms or ions of the catalyst surface. Direct measurements of chemisorption permits an evaluation of this stage in a catalytic process. The vast majority of investigations of chemisorption have been carried out with metals as the adsorbent; silica gel, aluminum oxide, and silica-alumina are the oxides which have been studied in the greatest detail. Along this line, a series of investigations [1-3] have shown that alcohols chemisorb on metal oxides at room temperature. The amount of alcohol chemisorbed depends on the chemical nature of the oxide [4, 2] and on the degree of dehydration of the surface [3]. The amount of alcohol chemisorbed increases with an increase in the degree of dehydration of the surface. The following scheme has been proposed for the chemisorption of alcohol [3, 5]:

On a hydrated surface:

$$-\overset{|}{\underset{|}{Si}}-OH + RCH_2OH \rightleftarrows -SiOR + H_2O. \quad (1)$$

On a dehydrated surface:



(2)

It has also been shown [6] that surface alcoholates are formed during adsorption of methanol on Al_2O_3 and on silica-aluminas. Measurements of the chemisorption of isopropyl alcohol on catalysts – iron oxide-alumina gels – led us to a similar conclusion [7].

Having at our disposal a series of promoted γ-alumina catalysts in which the second component was NiO, Fe_2O_3, Cr_2O_3, or ZrO_2, i.e., oxides of metals of different valence, we decided to measure the chemisorption of isopropyl alcohol on them, since the activity of these catalysts for the decomposition of isopropyl alcohol had previously been determined [8-11] and since the change in activity, selectivity, and phase composition of these catalysts with the introduction of a third component – K_2O – had been investigated in our laboratory. The results of this last investigation are the subject of a separate investigation.

The present work had the following aims: a) to compare the adsorption properties, particularly with respect to the chemisorption of isopropyl alcohol, of binary catalysts containing γ-Al_2O_3 but differing in the promoter, and b) to clarify the effect on chemisorption of the introduction of a third component – a base – into the above catalysts.

EXPERIMENTAL

The binary catalysts were prepared* by coprecipitation of the hydroxides from a mixture of solutions of the nitrates of aluminum and of the second metal using ammonia as the precipitant. The hydrogels were dried in air

*The binary catalysts were prepared by N. A. Pribytkova, who also determined their catalytic activity.

at 110° and then calcined in air for 6 hr at 600°. The catalysts containing the alkali promoter were prepared by impregnating the previously prepared binary catalysts with a solution of KNO_3 and calcining again at 600° in air. The compositions of the binary catalysts (in mole %) are shown in the table. The K_2O promoter amounted to 3 wt. % in all cases, calculated on the binary catalyst.

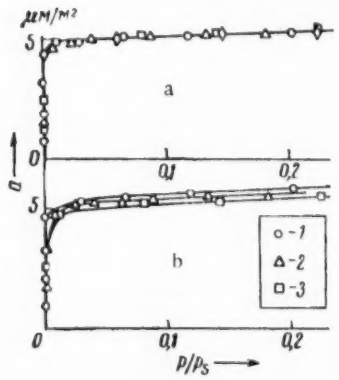
Catalyst composition	Surface area, sq m/g		Vol. ads. in monolayer	Amt. chemisorbed alc., μM/sq m
	by C_6H_6 ads.	by N_2 ads.		
25% NiO, 75% Al_2O_3		165	4,9	
25% NiO, 0,75% Al_2O_3+3%K_2O	162	155	5,0	
15% ZrO_2, 85% Al_2O_3		220	4,9	4,1
15 ZrO_2, 85%Al_2O_3+3%K_2O	170	160	4,9	3,7
15% Cr_2O_3, 85% Al_2O_3	210		4,9	4,2
15% Cr_2O_3, 85% Al_2O_3 +3%K_2O	255		5,2	4,4
18%Fe_2O_3, 82% Al_2O_3 *	200		4,9	4,9

* Results taken from our paper [7].

The investigation of the adsorption of isopropyl alcohol was carried out at 30° in a gravimetric apparatus with a quartz spring balance. The surface area of the catalysts was determined by nitrogen adsorption at liquid nitrogen temperature and by benzene vapor adsorption at 20°. In calculating the surface areas by the BET method, the area of the nitrogen molecule was taken as 16.2 sq A and that of the benzene molecule as 41 sq A. The amount of chemisorbed alcohol was taken to be the amount which could not be removed from the catalyst by pumping at 30°. The data obtained in the investigation are reported in the figure and table.

DISCUSSION

It is apparent from an inspection of Fig. 1a that the adsorption isotherms for isopropyl alcohol were the same for all of the binary catalysts, since all of the points fall on a single curve. It is also apparent that the surface is filled at low relative pressures (of the order of 0.01), after which, adsorption over the range studied, up to $p/p_s = 0.3$, changed only slightly with pressure. Figure 1b shows that the introduction of a third component (K_2O) had almost no effect either on the form of the isotherm or on the amount of alcohol adsorbed in a monolayer. It follows from the data of the table that the amount of alcohol adsorbed at 30° was approximately the same for all catalysts, i.e., within the concentration limits studied, the introduction of the various promoters, including K_2O, into γ-Al_2O_3 had no effect on the amount of isopropyl alcohol chemisorbed. This, it would seem, is not in good accord with such large differences in the chemical compositions of the catalysts investigated; however, in interpreting the observed facts it is necessary to take into account phase composition as well. It has previously been shown [9] that ZrO_2 is present in a mixed catalyst as an amorphous phase, while catalysts containing NiO, Fe_2O_3, and Cr_2O_3 in concentrations such as those investigated in the present work are single phase; when added to γ-Al_2O_3, the oxides form a solid solution which retains the cubic spinel lattice [5, 12, 13]. It is precisely this circumstance which plays the decisive role in the present case.



Adsorption isotherms for isopropyl alcohol at 30° on binary (a) and ternary (b) catalysts: 1) Cr_2O_3–Al_2O_3 and Cr_2O_3–Al_2O_3–K_2O; 2) NiO–Al_2O_3 and NiO–Al_2O_3–K_2O; 3) ZrO_2 –Al_2O_3 and ZrO_2 –Al_2O_3–K_2O.

Since in the binary catalysts investigated in this work the structure of the crystal lattice is retained at these ratios of component concentrations regardless of the nature of the oxide added to the γ-Al_2O_3 and since, as has been shown in our laboratory, K_2O does not change the phase composition, it is clear that the number of oxygen ions per unit of surface area must be the same for all these catalysts. Consequently, their abilities to form surface alcoholates must be the same or close to it, as observed experimentally. Although the ZrO_2 catalyst was not single phase, it contained 85% Al_2O_3,

and the explanation just presented is applicable to Al_2O_3. It may be remarked that the explanation is in better accord with the formation of alcoholate by scheme 2, above, than with scheme 1, since there may have been differences in the degree of surface hydration (i.e., differences in the number of OH groups) in the catalysts investigated, which did have different chemical natures.

The fact that the introduction of K_2O had no appreciable effect on the amount of isopropyl alcohol adsorbed also supports scheme 2, as shown by the following considerations. The amount of OH groups on the zirconia-alumina catalyst after evacuation at 300° was 5.4 μequiv/sq m, as determined by loss in weight during calcination at 1100°. K_2O, which was present in the catalyst in an amount of 3 weight %, could react with 4 μequiv/sq m of OH groups by the exchange reaction $>AlOH + KOH \rightleftharpoons AlOK + H_2O$. If chemisorption of isopropyl alcohol proceeded by scheme 1, i.e., if chemisorption depended on the number of surface hydroxyl groups, then, obviously, replacement of 70% of the OH groups by OK should lead to a sharp decrease in the amount of isopropyl alcohol chemisorbed, and this was not observed in the experiment. We suggest that calcination of the catalysts at 600° caused rather considerable dehydration of the surface, so that it reacted by scheme 2. It does not follow from the above that we assert that scheme 1 is unrealistic; we say only that in the case we investigated, the mechanism represented by scheme 2 is undoubtedly the sharply predominant chemisroption mechanism.

According to the data reported in [8-11], conversions in the decomposition of isopropyl alcohol at 250-260° and a space rate of 2.3 hr^{-1} over the catalysts used as adsorbents in the present work were 85.8% (only dehydration) for $NiO-Al_2O_3$, 27% (26% dehydration and 1% dehydrogenation) for $Fe_2O_3-Al_2O_3$, 84% (only dehydration) for $ZrO_2-Al_2O_3$, and 34% (6% dehydration and 28% dehydrogenation) for $Cr_2O_3-Al_2O_3-K_2O$. Comparison of these results with the data on the chemisorption of the alcohol at low temperature shows that in the cases which we investigated chemisorption is not a factor determining catalyst activity and selectivity. Therefore, it is probable that under the conditions of the reactions at temperatures of 250-350° the mechanism of chemisorption is different.

It has thus been shown that for binary catalysts of Al_2O_3 with NiO, Fe_2O_3, and Cr_2O_3, in which these oxides are completely dissolved in the γ-Al_2O_3, the amount of chemisorbed iso-C_3H_7OH is the same and is determined by the phase composition (i.e., by the distribution of O atoms or ions in the crystal lattice) and not by the chemical composition of the catalysts. The introduction of a third component (K_2O) which does not change the phase composition has no effect on the amount of chemisorbed iso-C_3H_7OH.

The data indicate that the formation of alcoholate during chemisorption of iso-C_3H_7OH on the catalysts investigated in the present work is predominantly through interaction of the alcohol with surface oxygen ions and not with OH groups.

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THE NATURE OF THE GREEN LIGHT AND THE COMPOSITION OF THE PRODUCTS IN THE COMBUSTION OF BORON AT A TEMPERATURE OF 3100°K

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Up to the present time, the composition of boron-containing combustion products has not been established. In the presence of boron, flames emit an intense band spectrum in the region of 3700-6800 A [1]. These "fluctuation bands" have been ascribed to different molecules: BO [2], B_2O_3 [3], H_3BO_3 [4]. In 1958, A. A. Mal'tsev and V. M. Tatevskii [6] proposed that these fluctuation bands are due to the radical BO_2. This point of view found confirmation in the work of Kaskan and Millikan [6] and also in the work of A. A. Mal'tsev, V. K. Matveev and V. M. Tatevskii [7-9].

With the aim of establishing the nature of the fluctuation bands and the composition of the products from the combustion of boron, we have developed a method of investigation based on explosion in a bomb and a study of the dependence of absorption in the 5470 A band on the concentration of oxygen, water, and hydroxyl.

The investigation of the explosion spectra was carried out with an apparatus which was capable of simultaneously recording the absorption spectra and the explosion pressures. The spherical steel bomb used in the work had a centrally located igniter [10]. Light from the source – an SVDSh-500 mercury lamp – was passed through a quartz window in the bomb and was then focused on the entrance slit of a DMR-1 monochromator. In order to avoid superimposition of the radiation from the explosion on the absorption spectrum, radiation from the lamp was modulated with a rotating disc with a frequency of about 2500 cps, which was placed between the bomb and the mercury lamp. A FZU-18 photomultiplier tube was located at the outlet of the monochromator, and the resulting signal was amplified and fed to a cathode-ray oscilloscope (for visual observation) and to an oscillograph (for recording). The intensity of the source radiation after passing through the bomb and also the explosion pressure were continuously recorded on the drum of the oscillograph during the experiment. An IGI diaphram indicator served as the pressure transducer [10].*

A mixture of CO, O_2, H_2 and Ar burned in the bomb. The temperature, T_e, and the composition of the combustion products at the time of maximum pressure, P_e, were calculated by known methods [11]. Into this original mixture were introduced small amounts of diborane (from 0.1 to 0.3 mole per 100 moles of the original mixture), which had almost no effect on the value of the maximum pressure P_e nor on the concentration of oxygen, water, or hydroxyl. The dependence of absorption in the 5470-A band on the amount of diborane added was studied with mixtures of different original compositions. The absorption was measured at the instant maximum explosion pressure was attained. Figure 1 shows the oscillogram recording the pressure and the absorption explosion spectrum for one of the experiments. The pressure curve is readily apparent. The amplitude of sinusoidal curve 2 is proportional to the intensity of the light passing through the bomb, and the separate trace (curve 3) was used to mark the instant of ignition of the combustible mixture by a spark from an induction coil.

In the case of boron-containing mixtures, the following boron-containing products could exist at the time of maximum pressure: B_2O_3, B_2O_2, BO, BO_2, and HBO_2. The concentrations of these products are interconnected by four equilibrium constant equations and one material balance equation.

* The authors take this opportunity to thank the Collective of the Laboratory of the Institute of Fossil Fuels, Academy of Sciences USSR, for making it possible for us to carry out the present work in a spherical bomb.

$$B_2O_3 \rightleftarrows B_2O_2 + {}^1/_2\,O_2,\quad K_1 = \frac{m_{B_2O_2}\cdot m_{O_2}^{1/2}}{m_{B_2O_3}}\cdot A; \tag{1}$$

$$B_2O_2 \rightleftarrows 2BO,\quad K_2 = \frac{m_{BO}^2}{m_{B_2O_2}}\cdot A^2; \tag{2}$$

$$BO_2 \rightleftarrows BO + {}^1/_2\,O_2,\quad K_3 = \frac{m_{BO}\cdot m_{O_2}^{1/2}}{m_{BO_2}}\cdot A; \tag{3}$$

$$HBO_2 + OH \rightleftarrows BO_2 + H_2O,\quad K_4 = \frac{m_{BO_2}\cdot m_{H_2O}}{m_{HBO_2}\cdot m_{OH}}; \tag{4}$$

$$2m_{0\,B_2H_6} = a = 2m_{B_2O_3} + 2m_{B_2O_2} + m_{BO} + m_{BO_2} + m_{HBO_2}, \tag{5}$$

where,

$$A = \sqrt{\frac{P_0 T_e}{100 T_0}}. \tag{6}$$

In the above equations, $\underline{m}$ denotes the number of moles of product calculated for 100 moles of the original mixture; $m_{0B_2H_6}$ is the number of moles of diborane per 100 moles of the original mixture; P_0 and T_0 are the initial pressure and temperature and $\underline{a}$ is the number of gram-atoms of boron per 100 moles of the original mixture. The K's in Eqs. (1)-(4) are all K_p's. A is the conversion factor from partial pressure to number of moles.

The initial and final compositions of the mixtures investigated (not taking into account the boron) are shown in Table 1. The initial compositions were calculated so that the same final temperature, T_e = 3080°K, was reached in all explosions. We assumed that the fluctuation bands are due either to B_2O_3 or to BO_2. Using the system of Eqs. (1)-(5), we were able to express $\underline{a}$ as a function of either of the concentrations m_{BO_2} or $m_{B_2O_3}$:

$$a = \left(1 + \frac{K_3}{A m_{O_2}^{1/2}} + \frac{1}{K_4}\cdot\frac{m_{H_2O}}{m_{OH}}\right) m_{BO_2} + \frac{2K_3^2}{K_2}\cdot\frac{1}{m_{O_2}}\left(1 + \frac{A m_{O_2}^{1/2}}{K_1}\right) m_{BO_2}^2, \tag{7}$$

$$a = 2\left(1 + \frac{K_1}{A m_{O_2}^{1/2}}\right) m_{B_2O_3} + \frac{\sqrt{K_1 K_2}}{A^{3/2} m_{O_2}^{1/4}}\left[1 + \left(\frac{1}{K_4}\cdot\frac{m_{H_2O}}{m_{OH}} + 1\right)\frac{A m_{O_2}^{1/2}}{K_3}\right] m_{B_2O_3}^{1/2} \tag{8}$$

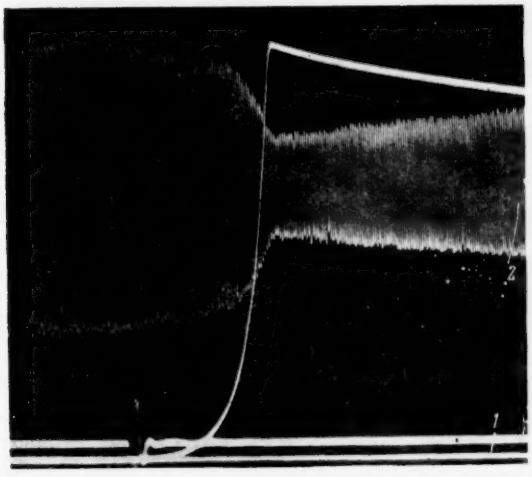

Fig. 1.

For each of the mixtures shown in Table 1 we selected experimentally those values of the amount of diborane, a, at which the absorption was the same for all mixtures (here and in the future, "absorption" will refer only to that at maximum explosion pressure). Table 2 presents the values of a for which absorption was the same for all mixtures. The optical density was 0.434.

TABLE 1. P_0 = 500 mm Hg, T_0 = 293°K, T_e = 3080°K

Expt. No.	$m_{0\,H_2}$	$m_{0\,O_2}$	$m_{0\,CO}$	$m_{0\,Ar}$	$m_{0\,N_2}$	m_{H_2}	m_H	m_{H_2O}
2,2	2,651	16,123	47,000	33,505	0,721	0,235	0,367	1,749
2,3	6,121	16,560	42,368	34,270	0,681	0,602	0,588	4,455
2,4	9,404	16,861	37,660	35,437	0,638	0,964	0,774	7,099
10,2	6,096	25,990	32,599	34,581	0,735	0,298	0,414	4,448
10,4	19,579	27,382	17,500	34,863	0,676	1,081	0,788	16,035

Expt. No.	m_{OH}	m_{O_2}	m_o	m_{CO}	m_{CO_2}	m_{NO}	m_{N_2}
2,2	0,968	2,631	0,904	23,802	23,197	0,165	0,695
2,3	1,541	2,602	0,900	21,508	20,861	0,165	0,599
2,4	1,940	2,574	0,895	19,175	18,495	0,158	0,500
10,2	2,205	10,765	1,829	10,969	21,631	0,327	0,572
10,4	4,139	10,446	1,802	5,948	11,551	0,303	0,522

Note: Compositions are given in moles per 100 moles of the original mixture.

TABLE 2

Mixture No.	a	m_{H_2O}/m_{OH}
2,2	0,159	1,807
2,3	0,200	2,891
2,4	0,258	3,659
10,2	0,159	2,035

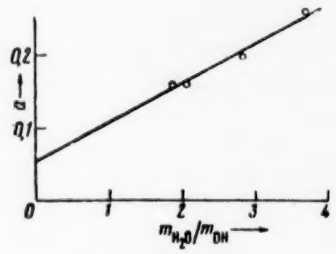

Fig. 2.

It follows from the data of Table 2 that a linear relationship exists between the experimental values of a and the ratio m_{H_2O}/m_{OH}

$$a = 0{,}0544\,\frac{m_{H_2O}}{m_{OH}} + 0{,}0497. \qquad (9)$$

This relationship is depicted in Fig. 2. At the same time, no such relationship was observed between the experimental values of a and m_{O_2}.

Let us compare the data of Table 2 and the experimental relationship (9) with the theoretical expressions (7) and (8). The experimental conditions were such that absorption was the same for all values of a, m_{O_2}, and m_{H_2O}/m_{OH}. If the absorption were due to BO_2 then m_{BO_2} in (7) would be constant, while if the absorption were due to B_2O_3 then $m_{B_2O_3}$ in (8) would be constant. The experimental relationship (9) corresponds to theoretical expression (7) provided the spectrum is due to the BO_2 radical and provided the basic combustion products of diborane are BO_2 and HBO_2. In this case, Eq. (7) assumes the form

$$a = \frac{m_{BO_2}}{K_4} \cdot \frac{m_{H_2O}}{m_{OH}} + m_{BO_2}, \qquad (10)$$

which is in complete agreement with experimental Eq. (9). From a comparison of (9) and (10) it is possible to determine K_4 and the absolute concentration m_{HBO_2}, where $K_4 = 0.9$.

On the other hand, in no case does the experimental relationship (9) satisfy Eq. (8). This means that the observed spectrum cannot be ascribed to the B_2O_3 molecule. This is also indicated by the absence of any connection between the experimental values of $\underline{a}$ and the oxygen concentration m_{O_2}. Nor can the experimental relationship (9) be explained on the assumption that the spectrum is due to BO or B_2O_2 molecules.

Thus, the results of the present work confirm the conclusions of A. A. Mal'tsev and V. M. Tatevskii and of Millikan that the fluctuation bands are due to the BO_2 radical.

It was established that the major boron-containing products of combustion under our experimental conditions, including a temperature of 3080°K, are HBO_2 and BO_2.

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ON THE CATALYTIC HYDROGENATION OF ESTERS

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The tendency of carboxyl groups to undergo catalytic hydrogenation is less than that of olefinic and carbonyl bonds. As a rule, catalytic hydrogenation of esters of unsaturated acids converts them to the corresponding esters of saturated acids. Thus, for example, vapor-phase hydrogenation of esters of acrylic acid over nickel catalyst at 180° yields esters of propionic acid [1]. Vapor-phase hydrogenation of amyl oleate over platinized asbestos yields analogous results. In this case too, only the olefinic bond is hydrogenated, and amyl stearate is formed [2].

We have recently obtained experimental data showing that under vapor-phase hydrogenation conditions over platinum, hydrogenolysis of the ether bond of a furan ring takes place more readily than does hydrogenation of a carbalkoxy group [3]. All of these results demonstrate the high stability of the carboxyl group with respect to catalytic hydrogenation reactions. As a matter of fact, successful hydrogenation of ester groups has been found possible only at elevated hydrogen pressure [4]. It was found that esters are reduced to two alcohols according to the reaction

$$RCOOR' \xrightarrow{H_2} RCH_2OH + R'OH.$$

This reaction proceeds most smoothly over copper chromite. For example, hydrogenation of ethyl valerate over copper chromite at 250° and 220 atm pressure gives a 94% yield of amyl alcohol [4].

The search for conditions under which catalytic hydrogenation of esters can be accomplished can provide only a partial solution of the more general problem of the catalytic hydrogenation of carbalkoxy groups. In its more general form, the question may be posed as follows: what kind of conversions is the carbalkoxy groups capable of under catalytic hydrogenation conditions? With this aim, we undertook, first, an investigation of the action of various catalysts on the carbalkoxy group during vapor-phase hydrogenation at atmospheric pressure, and then the effect of hydrogen pressure and temperature was studied in certain cases. Our results can be explained by relating them to the specificness of action of the catalysts, on one hand, and to hydrogen pressure, on the other. Depending on these conditions, the carbalkoxy group can undergo hydrogenation by two courses: it may be reduced so that two alcohols are formed from the ester, or it can undergo hydrogenolysis forming a carboxyl group and a hydrocarbon:

$$R-\underset{\underset{O}{\|}}{C}-O-R' \xrightarrow{H_2} \begin{cases} \longrightarrow RCH_2OH + R'OH \\ \longrightarrow RCOOH + R'H \end{cases}$$

Hydrogenolysis of the ester group takes place smoothly over platinum and palladium catalysts when the hydrogenation is carried out at atmospheric pressure. Of these two catalysts, platinum is the more active. At 300°, hydrogenolysis of esters over Pt–C goes practically to completion, while conversion of the ester is about 65% over Pd–C under the same conditions.

$$CH_3COO\vdots R \xrightarrow[300^\circ]{H_2;\,Pt-C} CH_3COOH + RH,$$

$$R = n\text{-}C_5H_{11},\ n\text{-}C_6H_{13},\ n\text{-}C_7H_{15};$$

$$CH_3CH_2CH_2COO\vdots \text{iso-}C_5H_{11} \rightarrow CH_3CH_2CH_2COOH + \text{iso-}C_5H_{12}.$$

Temperature has a substantial effect on the hydrogenolysis of esters. Thus, only very slight conversion of the ester to acid and hydrocarbon is observed at 250°.

It is well known from the work of Sabatier and Mailhe [5] that esters can undergo decomposition to an acid and an ethylenic hydrocarbon. It might be assumed that this reaction also takes place during hydrogenation of esters under the conditions of our experiments and that, consequently, the formation of the paraffinic hydrocarbon takes place as a result of hydrogenation of the ethylenic hydrocarbon. However, an investigation of the behavior of isoamyl butyrate over Pt–C at 300° in the absence of hydrogen showed that isopentene is formed in an amount of not more than 3-4% under these conditions. Consequently, the formation of paraffinic hydrocarbons takes place as a result of direct hydrogenolysis of the C–O bond in the carboxyl group. Moreover, in addition to the catalyst, the hydrogen pressure under which the hydrogenation is carried out has s substantial effect on the course of the conversion of esters. Thus, over Pt–C at 50 atm pressure and 350° hexyl acetate undergoes not only hydrogenolysis but also reduction of the carbalkoxy group, as shown by the presence in the catalyzate of acetic acid, hexane, and pentane. The formation of pentane is possibly the consequence of successive reactions – the dehydrogenation of hexyl alcohol to the corresponding aldehyde and decarbonylation of the latter to pentane. Thus, hydrogenation of esters over platinum catalyst at elevated hydrogen pressure is not selective, though it is at atmospheric pressure.

The opposite relationship between hydrogen pressure and selectivity of the conversion of the carboxyl group is observed with Cu–Al catalyst; selective conversion takes place only at elevated hydrogen pressure with the formation of hydroxyl groups, while at ordinary pressure other conversion occur with the formation of a complex mixture of paraffinic and olefinic hydrocarbons.

$$CH_3COOR \xrightarrow[300°,\ 50\ atm.]{H_2;\ Cu-Al} ROH + C_2H_5OH$$
$$R = C_5H_{11},\ C_6H_{13}$$

The properties of skeletal Ni–Al catalyst were investigated with respect to the hydrogenation of amyl acetate and hexyl acetate at atmospheric pressure and temperatures of 250 and 300°. The conversion of hexyl acetate at 250 and 300° was 30 and 80%, respectively. Predominantly hexane with a small amount of hexenes is formed from hexyl acetate at 250°. At 300°, the catalyzate from hexyl acetate contains only a very small amount of pentane and pentenes. These data show that at atmospheric pressure, skeletal Ni–Al catalyst promotes hydrogenolysis of the carbalkoxy group, though less smoothly than platinum and palladium. The results of our investigations permit the following conclusions.

Catalytic hydrogenation of esters in the vapor phase can lead either to reduction of the ester to two alcohols or to hydrogenolysis with the formation of an acid and a paraffinic hydrocarbon. The first of these reactions is favored by elevated hydrogen pressure. Skeletal copper proved to be the most effective catalyst for the reduction of esters. On the contrary, hydrogenolysis of esters proceeds smoothly over platinized and palladinized carbon at ordinary pressure. Hydrogenation of the esters was carried out in a flow-type apparatus at a space rate of 0.15 hr^{-1} and at both ordinary and elevated pressures.

The alkyl acetates were prepared by heating the alcohols with excess acetic anhydride in the presence of freshly fused sodium acetate.

The catalysts – platinized carbon, palladinized carbon, skeletal nickel–aluminum, and skeletal copper–aluminum – were prepared by the method described previously [6]. The catalyzates were distilled in a column, and the reactions products were identified by determination of their physical constants and by gas–liquid chromatography.

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THERMODYNAMIC PROPERTIES OF Ag-Sb ALLOYS

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To determine the thermodynamic properties of Ag-Sb alloys we have studied the relation between the electromotive force (EMF) and the temperature for the following electrical system:

$$Ag_{(s)} \mid Ag^{+}_{(\text{in melt: KI+NaI+AgI})} \mid Ag - Sb_{(\text{alloy})}.$$

Experiments were carried out at 630-830°C in an atmosphere of nitrogen. In all, eight alloys were studied, their compositions falling within the limits 10.3-79.5 atoms % of silver. The methods of carrying out the experiments and calculating the results have been described earlier [1]. The experimental data are cited in the table.

Experimental Data for Liquid Alloys of Silver and Antimony at 1000°K

N_{Ag}	E, mv	dE/dT, mv/100°	a^{*}_{Ag}	$\Delta\bar{H}^{*}_{Ag}$, kcal/g.at.	$\Delta\bar{S}^{*}_{Ag}$, e.u./g.at.	a_{Ag}**	$\Delta\bar{H}^{**}_{Ag}$, kcal/g.at.	$\Delta\bar{S}^{**}_{Ag}$, e.u./g.at.
0,103	202,4	41,1	0,095	4,66	9,48	0,074	1,97	7,30
0,203	161,0	31,5	0,154	3,55	7,26	0,119	0,86	5,08
0,295	139,0	26,0	0,199	2,79	6,00	0,154	0,10	3,82
0,395	120,4	21,7	0,247	2,24	5,00	0,192	—0,45	2,82
0,498	103,7	17,6	0,300	1,66	4,06	0,232	—1,03	1,88
0,613	86,8	13,8	0,365	1,18	3,18	0,283	—1,51	1,00
0,694	61,8	10,2	0,488	0,92	2,36	0,378	—1,77	0,18
0,795	23,2	10,0	0,764	1,78	2,31	0,591	—0,91	0,13

* Standard state – solid silver and liquid antimony.

** Standard state – liquid components, for calculations on liquid silver the latent heat of fusion of silver is taken to be −2.69 kcal/g-atom, m. p. 1234°K [4].

A complete thermodynamic description of the system Ag-Sb in the liquid state was undertaken first – determination of the isobaric potential, enthalpy and entropy of formation of the alloy. Electrolytic molten sodium and potassium iodides were used, to which was added a small quantity of silver iodide to prevent the electrochemical reaction which occurred when molten chlorides [2] were used as the electrolyte. As a result the reproducibility of the EMF for each alloy in our experiments was in the limits of ± 0.5%.

The energies of formation of the Ag-Sb alloys at 1000°K are shown in Figs. 1 and 2. In general the system is characterized by a negative deviation from Raoult's law (see Fig. 1), a negative ΔZ^{izb}*, a positive ΔS^{izb} and a complex curve of the enthalpy of formation (Fig. 2). This agrees with the phase diagram which in the region lying close to (100%) silver is complicated enough [3]. In these figures we have given for comparison the corresponding values for Cu - Sb alloys which we determined earlier.

The very great similarity in character of the corresponding curves is noteworthy; the minima in the ΔZ^{izb} and ΔH curves and the maximum in the ΔS^{izb} curve occur in both systems at alloys with an approximately equal antimony content. The character of the deviations from Raoult's law in these systems is very similar.

A sufficiently close agreement is also seen in the phase diagrams of both systems; the intermetallic phases are grouped on the copper or silver side and correspond to the phases Ag_3Sb and Cu_3Sb. However they have

* "izb" stands for "isobaric" throughout article.

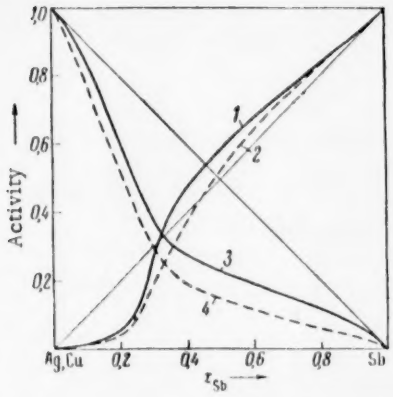

Fig. 1. Activities of the components in the systems Ag-Sb and Cu-Sb at 1000°K. 1,3) Ag-Sb system: 1) a_{Sb}, 3) a_{Ag}. 2,4) Cu-Sb system: 2) a_{Sb}, 4) a_{Cu}.

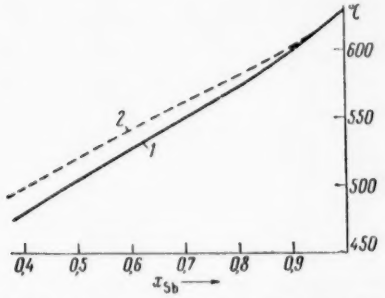

Fig. 3. Comparison of the experimental [8, 9] (1) and calculated (2) liquidus curves for the system Ag-Sb.

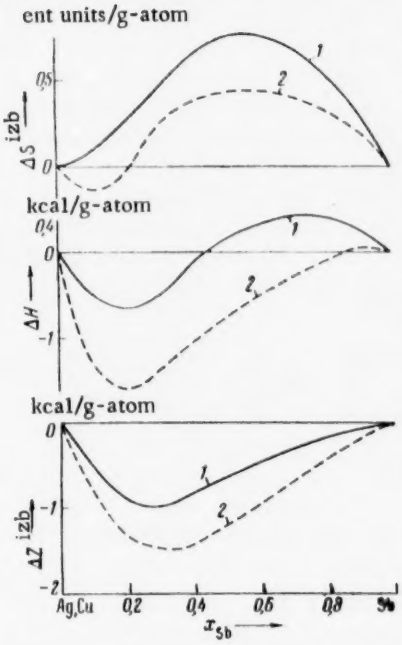

Fig. 2. Comparison of the thermodynamic properties of the systems Ag-Sb and Cu-Sb at 1000°K. 1) Ag-Sb system; 2) Cu-Sb system.

differences; firstly the number of phases in the Cu-Sb system is noticeably greater, which is evidence of the greater intensity of reaction between the components in this system—this is also reflected in the thermodynamic properties (see Fig. 2); secondly, the intermetallic compound in the Cu-Sb system begins to appear at a higher antimony content; this corresponds to Cu_2Sb for which there is no evidence in the Ag-Sb system. In this connection it is interesting to look at the character of the change in antimony activity in relation to composition (Fig. 1). In both systems the positive deviation from Raoult's law at low antimony content changes to a negative one, but in the Cu-Sb alloys the change occurs earlier. This effect is connected with the formation in the alloy not only of groups of the type A-B but also of A_2-B and even A_3-B. It is true that in the Ag-Sb alloy the tendency to form the group A_3-B is expressed more strongly compared with A_2-B or A-B, then in the Cu-Sb alloys where it is evident that the groups A_2-B and A-B are present considerably more than A_3-B. The phase diagram shows this indirectly; in the Ag-Sb system compounds analogous to Cu_2-Sb are absent, as indeed are compounds with a lower content of silver than the phase Ag_3Sb. It is possible that the complex relation between the enthalpy of formation and composition of Ag-Sb alloys is connected with this effect.

By obtaining the known thermodynamic position of the equilibrium activity of the component in the phases at equilibrium one can calculate the phase diagram of the given system. We carried out such a calculation for the Ag-Sb system to determine the liquidus curve from antimony to the eutectic. We earlier carried out a similar calculation for the Cu-Sb system [6] and the results are cited in Fig. 3. The calculated and experimentally determined [7, 8] liquidus curves agree well, but the calculated one lies somewhat higher (about 10°). This is evidently connected with the nonlinear dependence of log a_{Sb} and 1/T which was observed in the Au-Sn system by Kleppa [9]. It is possible that, the packing of the atoms in the liquid phase changes close to the liquidus curve and this ought to affect the entropy of mixing and consequently the temperature coefficient dE/dT. In the experimental conditions (high temperature, molten electrolyte) we could not study the activity of the components sufficiently close to the liquidus curve.

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2-PHENYL-4,5,6,7-TETRAHYDROINDANDIONE-1,3

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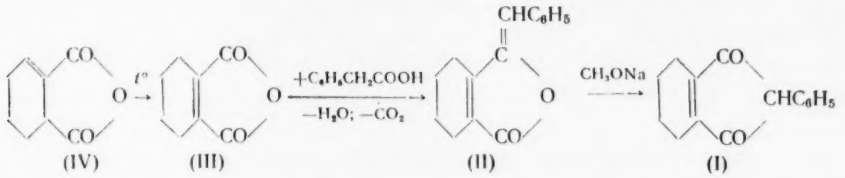
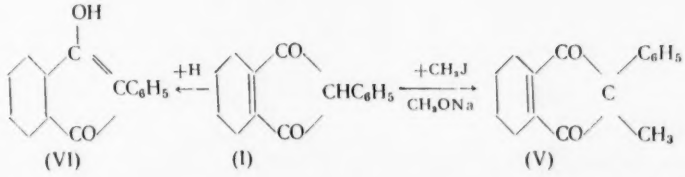
Continuing a study of the relation between structure and properties in a series of indandiones-1,3, we recently reported on a study of the prototype of the indandione system – cyclopenten-4-dione-1,3 [1, 2]. The present paper is concerned with a new indandione-1,3 analogue, 2-phenyl-4,5,6,7-tetrahydroindandione-1,3 (I).

This compound was obtained in 1935 by Berlingozzi and Senatori [3] but they did not study it closely and ascribed an incorrect structure to it. We obtained I by a method analogous to the synthesis of 2-arylindandiones-1,3, namely the thermal condensation of $\Delta^{1,2}$-tetrahydrophthalic anhydride (III) with phenylacetic acid to give the corresponding benzaltetrahydrophthalide (II), which rearranged into 2-phenyl-4,5,6,7-tetrahydroindandione-1,3 (I) with sodium methoxide. II was also obtained by the thermal condensation of $\Delta^{2,3}$-tetrahydrophthalic anhydride (IV) with phenylacetic acid; this reaction evidently goes by the long known thermal isomerization IV into III [4, 5]. This explanation was taken into account by Berlingozzi and Senatori, who carried out condensation with IV [3, 6], and they were led in this way to an incorrect conclusion about the position of the double bond in II and in I.



2-Phenyl-4,5,6,7-tetrahydroindandione-1,3 (I) is a light yellow substance which dissolves in alkalies to give a deep violet color. It gives a colorless dioxime. Thanks to the stability of (I) in base we easily succeeded in alkylating it in a basic medium, a reaction which is not possible for cyclopenten-4-dione-1,3 [1, 2]. By heating I with an equivalent quantity of methyl iodide and sodium methoxide we obtained the 2-methyl derivative (V) in almost quantitative yield. This reaction proceeded easily at room temperature even on shaking I with methyl iodide in the presence of calcium oxide. Reduction of I with zinc and acetic acid or catalytic hydrogenation in the presence of finely divided nickel gave 2-phenylhexahydroindandione-1,3 (VI). Besides VI a thick oil was also isolated, evidently the product of further reduction.



The IR spectra of the compounds obtained were recorded (see the table). Only normal carbonyl and double bonds were found in the spectrum of I. A similar spectrum was obtained for V. It is interesting to note that the carbonyl frequencies of I and V are noticeably lower than those found for 2-phenylindandione-1,3 and 2-methyl-2-phenylindandione-1,3; this agrees with the general rule for substituent of an aromatic ring at a double bond. The IR spectral curves of I and V and the absence of absorption in the O–H bond vibration region excludes the possibility of the existence of I in the enol form and confirms its diketone structure. Weak bands appear in the spectra of solid around 3400 cm^{-1}. These are evidently overtones of the carbonyl vibration similar to [1].

2-Phenylhexahydroindandione-1,3 (VI) on the other hand differs markedly from I both in its chemical properties and in its structure. The infrared spectrum of VI is characteristic of a completely enolized β-diketone – it contains not a single band which could be attributed to ν CO in the dicarbonyl form of VI [7, 8]. Thus in the spectrum of solid VI a broad band at 2640-2660 cm^{-1} was observed, which is found in many enolized β-diketones with strong hydrogen bonds (e.g., dimedone [9]). This confirmed that solid VI occurs exclusively in the strongly associated enolized form. The dicarbonyl form of VI was not observed in solution in dichloroethane and alcohol. Unfortunately we were not able to study VI in less polar solvents because of its low solubility.

The IR spectra showed that compounds of the cyclopenten-4-dione-1,3 [1] and 4,5,6,7-tetrahydroindandione-1,3 systems, like indandione-1,3 [10], are not tautomeric and exist solely in the dicarbonyl form. On the other hand, cyclopentandione-1,3 [2], hexahydroindandione-1,3 [11], and $\Delta^{5,6}$-tetrahydroindandione-1,3 [2] are tautomeric substances which exist characteristically in the enol form (similar to the six-membered cyclic β-diketone).

To confirm the structure of II the IR spectra of II and 3-benzalphthalide were recorded. Besides the high frequency of the lactone carbonyl [12] two double bond bands appeared in the spectrum of II. The higher (1660 cm^{-1}) of these, which is found also in the spectrum of the 3-benzalphthalide, evidently corresponds to the vibration of an exocyclic double bond; and the lower, which is found only in the spectrum of II, to the vibration of an endocyclic bond.

EXPERIMENTAL

3-Benzal-4,5,6,7-tetrahydrophthalide (II). a) In a flask fitted with a thermometer and an outlet tube (for distilling out the water formed in the reaction) 45 g $\Delta^{1,2}$-tetrahydrophthalic anhydride (III) [15], 2.5 g anhydrous sodium acetate, and 45 g phenylacetic acid were heated on a metal bath initially at 180°, raised gradually to 200° (in the flask). Two portions (2.5 g in all) of sodium acetate were added during the reaction. When about half the calculated quantity of water had distilled the temperature was gradually raised to 210°. When the calculated quantity of water (about 5.5 ml) had separated the orange-red mass was cooled to 100-110°, poured into 200 ml methanol and kept in the refrigerator overnight. The orange yellow crystals were washed with a small quantity of cold methanol. The yield of crude II was 30.5 g (46%) – crude II was good enough for the preparation of I. A small amount of II separated from the filtrate, raising the overall yield to 55% m. p. 117°.

b) In a similar way II (m. p. 117-118°) was obtained from 0.43 g $\Delta^{2,3}$-tetrahydrophthalic anhdride (IV) [5], 0.5 g phenyl acetic acid, and 0.1 g anhydrous sodium acetate which were heated at 180-190° for 20 min. To purify crude II it was shaken with a dilute solution of sodium methoxide and the residue crystallized from methanol, or petroleum ether. White crystals, m. p. 118°.

Found %: C 79.72; H 6.30. $C_{15}H_{14}O_2$. Calculated %: C 79.64; H 6.23.

The dioxime was prepared from 0.5 g substance I, 0.4 g $NH_2OH \cdot HCl$ and 0.5 g CH_3COONa diluted with methanol. White crystals, 0.25 g, m. p. 260° (from methanol).

Found %: N 11.011. $C_{15}H_{16}O_2N_2$. Calculated %: N 10.93.

2-Methyl-2-phenyl-4,5,6,7-tetrahydroindandione-1,3 (V). 3 g I was boiled with sodium methoxide (from 0.31 g sodium) and 1.2 ml CH_3I in 50 ml methanol. After some minutes the deep violet color of the solution changed to orange. The cooled solution was poured into water and kept in the refrigerator. The precipitated crystals (3 g, 94%) were recrystallized from methanol or aqueous methanol to give yellow crystals, m. p. 94-95°.

Found %: C 80.29; H 7.00. $C_{16}H_{16}O_2$. Calculated %: C 79.98; H 6.71.

2-Phenylhexahydroindandione-1,3 (VI). a) 1.5 g I was heated in glacial acetic acid on a boiling water bath with zinc powder until the solution no longer gave a violet color with alkali (characteristic test for I). It was then poured into water. The white precipitate was recrystallized from dilute alcohol or hexane. The yield was 0.3 g (20%), m. p. 229-230° (from $CHCl_3$).

b) 0.1 g I in ethanolic solution was hydrogenated in the presence of finely divided nickel and a small quantity of KI. The ethanol was evaporated in vacuum and the residue crystallized from $ChCl_3$. The product melted at 229° and gave no depression of the melting point with the product obtained in a).

Found %: C 78.79; H 7.23. $C_{15}H_{16}O_2$. Calculated: C 78.94; H 7.06.

Infrared Absorption Spectra

Compound	State of substance (solvent)				3000-3700 cm^{-1} region
2-Phenyl-4,5,6,7-tetrahydroindandione-1,3 (I)	Solid	a	1633 (76)	1693 (91) 1735 (48)	b, c
	$CH_2ClCHCl$ $4 \cdot 10^{-2}$ M	–	1638 (13)	1702 (82) 1745 (18)	–
2-Methyl-2-phenyl-4,5,6-tetrahydroindandione-1,3 (V)	Solid	a	1635 (76)	1691 (100) 1742 (64)	b
	CH_2ClCH_2Cl $6 \cdot 10^{-2}$ M	–	1637 (12)	1695 (93) 1740 (23)	–
2-Phenylindandione-1,3	Solid	1585 (42) 1602 shoulder	–	1708 (68) 1740 (40)	–
	$CHCl_3$ [13]	–	–	1712 1748	–
2-Methyl-2-phenylindandione-1,3	Solid [14]	1596 (68)	–	1710 (91) 1747 (58)	–
Dioxime of 2-phenyl-4,5,6,7-tetrahydroindandione-1,3	Solid	1608 (54)	1651 (57)	–	~3065 (62) ~3170 (55)
3-Benzal-4,5,6,7-tetrahydrophthalide (11)	Solid	a	1635 (75) 1660 (76)	1756 (97)	–
3-Benzalphthalide	Solid	1608 (43)	1660 (46)	1778 (84	–
2-Phenylhexahydroindandione-1,3 (VI)	Solid	1575 (80)	1584 (85)	1611 (68) 1661 (43)	2640–2660 (65) c
	CH_2ClCH_2Cl + + 10% C_2H_5OH $4 \cdot 10^{-2}$ M	1600 (44)	1631 (62)	1679 (42)	d

Notes: a) weak band at about 1600 cm^{-1}; b) weak band at about 3400 cm^{-1}; c) taken in the range 2500-3700 cm^{-1}; d) this region was not available because of solvent absorption.

All spectra were taken on a single beam instrument IKS-12 with a NaCl prism, in most cases in the ranges 1500-1760 and 3000-3700 cm^{-1}. The spectra of solid substances were obtained in paraffin oil. The positions of the bands are given in reciprocal centimeters and in brackets are given their relative intensities in percentage absorption.

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MECHANISM OF THE TRANSFORMATIONS OF CYCLOHEXENE AND 1,3-CYCLOHEXADIENE ON PLATINUM FILMS

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(Presented by Academician A. A. Balandin, January 10, 1961)
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The processes of hydrogen redistribution between molecules of the same compound, not accompanied by gas evolution, were discovered in 1911 and were subsequently studied in detail by N. D. Zelinskii and his school [1]. In particular, it was established that 1,3-cyclohexadiene is transformed at a rapid rate in accordance with the equation:

$$2C_6H_8 = C_6H_6 + C_6H_{10}. \quad (1)$$

while cyclohexene reacts much more slowly in accordance with the equation:

$$3C_6H_{10} = C_6H_6 + 2C_6H_{12}. \quad (2)$$

On the basis of the data available at the time, A. A. Balandin [2] made an attempt to explain the peculiarities of these reactions using models, and according to him a direct transfer of the hydrogen atoms between the molecules takes place either on one or, in the case of reaction (2), on two triplets. Later Linstead and his co-workers [3] also came to the same conclusion regarding the direct transfer of hydrogen, whereas N. A. Shcheglova and M. Ya. Kagan [4] believed that the redistribution of hydrogen in cyclohexene consists of separate stages of dehydrogenation and hydrogenation.

In view of the existence of several theories regarding the mechanism of the hydrogen redistribution it seemed desirable to obtain some data that would answer this problem in the most direct manner possible. The present paper is devoted to the results obtained in studying the transformations of cyclohexene and 1,3-cyclohexadiene* at 20° on platinum films, the electrical conductivities of which were measured during the course of the experiments.

The experimental procedure was the same as that used in previous papers [6-10], where it was shown that the adsorption of benzene, cyclohexane, cyclohexene, and 1,3-cyclohexadiene can be subdivided into stable, not removed by prolonged evacuation to $1 \cdot 10^{-7}$ mm at 20°, and reversible. In the first pass over freshly prepared platinum film all of the enumerated hydrocarbons exhibit stable adsorption and are dehydrogenated. Especially large amounts of hydrogen are evolved in the stable adsorption of cyclohexene and 1,3-cyclohexadiene.

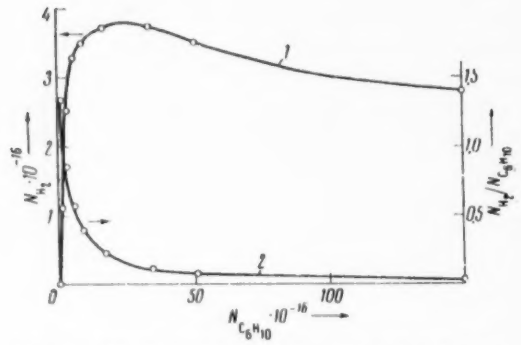
The reversible adsorption of benzene and cyclohexane is not accompanied by dehydrogenation, while both cyclohexene and 1,3-cyclohexadiene lose hydrogen even under these conditions, which is manifested by the appearance of a gas in the adsorption vessel that is not condensed at the temperature of liquid nitrogen and, as is shown below, hydrogenates cyclohexene. The changes in the electrical conductivity of the film during the reversible adsorption of cyclohexene also indicated the presence of hydrogen. Consequently, the evolution of hydrogen as the result of the stable adsorption of benzene and cyclohexane on platinum films is due to chemisorption, while in the case of cyclohexene and 1,3-cyclohexadiene it is a catalytic process, which takes place when the vapors are admitted after the evacuation of the film.

If the admittance of the cyclohexene or 1,3-cyclohexadiene vapors is discontinued periodically and the hydrocarbon vapors are removed from the gas phase by freezing, then it is possible to show that the amount of hydrogen formed passes through a maximum. In particular, using cyclohexene we obtained curve 1 in Fig. 1, while curve 2 shows the ratio of hydrogen to cyclohexene molecules $N_{H_2}/N_{C_6H_{10}}$, as a function of the amount of cyclohexene

*The constants of the hydrocarbons used – C_6H_{10}, b. p. 82.5°, $n^{20}D$ 1.4448, d^{20}_4 0.812; C_6H_8, b. p. 78.5°/740 mm, $n^{20}D$ 1.4740 – showed satisfactory agreement with the literature data [5] – C_6H_{10}, b. p. 83°, $n^{20}D$ 1.44507, d^{20}_4 0.8102; C_6H_8, b. p. 80.5°, $n^{20}D$ 1.4744.

molecules passed in. The results of the experiments using 1,3-cyclohexadiene were analogous, but here the hydrogen evolution was approximately only half that deriving from the adsorption of a corresponding amount of cyclohexene. Thus, after the passage of $1 \cdot 10^{17}$ molecules of cyclohexene over a film, containing $3.5 \cdot 10^{16}$ atoms of platinum per sq cm, the pressure of the liberated hydrogen was $2.5 \cdot 10^{-3}$ mm. To obtain a closely similar pressure ($2 \cdot 10^{-3}$ mm) required the passage of $2.1 \cdot 10^{17}$ molecules of 1,3-cyclohexadiene over the same film after its evacuation.

To determine the reasons for the decrease in the ratio $N_{H_2}/N_{C_6H_{10}}$ with increase in $N_{C_6H_{10}}$ we ran a series of experiments, where in each experiment $2.8 \cdot 10^{16}$ molecules of cyclohexene was passed at a constant rate of $1.4 \cdot 10^{15}$ molecules/min into the vessel containing the platinum film, and also various amounts of hydrogen. The results of the experiments using a film with a density of $2.2 \cdot 10^{16}$ atoms Pt/sq cm are given in the table. In all of the experiments except No. 10, the vessel was evacuated in advance to a residual pressure of about $5 \cdot 10^{-7}$ mm.



Amount of hydrogen formed N_{H_2} (1) and ratio N_{H_2} per $N_{C_6H_{10}}$ (2) as functions of amount of cyclohexene $N_{C_6H_{10}}$ passed into the vessel containing the film.

Experiment Nos. 1 and 2 show the reproducibility of the degree of cyclohexene dehydrogenation. From Expt. Nos. 3-10 it can be seen that with a certain amount of hydrogen in the adsorption vessel, which in the given case was close to $7.9 \cdot 10^{16}$ molecules, the passage of $2.8 \cdot 10^{16}$ molecules of cyclohexene fails to lead to either the liberation or the absorption of hydrogen. If the amount of hydrogen is either less or greater than this amount, then when cyclohexene is admitted the hydrogen is respectively either liberated or it is absorbed. 1,3-Cyclohexadiene is also capable of both dehydrogenation and hydrogenation on platinum film at 20°. Thus, in one of the experiments, after the passage of $1.5 \cdot 10^{17}$ molecules of 1,3-cyclohexadiene, the hydrogen pressure in the adsorption vessel containing the platinum film increased from $8 \cdot 10^{-4}$ to $2 \cdot 10^{-3}$ mm, while in the case where the hydrogen pressure over the same film before the admittance of the hydrocarbon was $1.2 \cdot 10^{-2}$ mm, it dropped to $9 \cdot 10^{-3}$ mm after the admittance of $2.0 \cdot 10^{17}$ molecules of 1,3-cyclohexadiene.

These results show that both cyclohexene and 1,3-cyclohexadiene exhibit simultaneous hydrogenation and dehydrogenation on platinum films at 20°. Dehydrogenation predominates during the admittance of the first portions of these hydrocarbons, but as the amount of hydrogen accumulates the hydrogenation rate increases. If the rates of these processes were to be compared, then the amount of hydrogen in the vessel, having reached a certain value, would not change as more hydrocarbon is admitted. However, actually (see figure, curve 1) the amount of hydrogen passes through a maximum. Consequently, the ratio of the hydrogenation rate to the dehydrogenation rate increases. The results of Expt. Nos. 7-10 (Table 1) testify to this. In Expt. Nos. 7-9 the hydrogen consumption decreased steadily with decrease in the initial amount of hydrogen, while in Expt. No. 10, where a further decrease should have been observed, there occurred an increase in the hydrogen consumption. As had already been mentioned, the products of Expt. No. 9 were not evacuated prior to Expt. No. 10.

It is natural to assume that the predominance in the hydrogenation rate of either cyclohexene or 1,3-cyclohexadiene over the dehydrogenation rate, observed when using certain amounts of the hydrocarbons, is due to a selective blocking of those portions of the film surface where dehydrogenation takes place. Both dehydrogenation and hydrogenation take place in the reversible adsorption of either cyclohexene or 1,3-cyclohexadiene, where decyclization and cracking are not very probable reactions. Under these conditions only benzene and cyclohexane can be the stable transformation products, which during reversible adsorption on platinum films at 20° are not dehydrogenated. Consequently, the effect of their presence on the ratio in the rates of the hydrogenation and dehydrogenation of cyclohexene had to be determined.

For this purpose we ran some experiments, which differed from those given in Table 1 in that a definite hydrogen pressure was first established in the vessel with the platinum film, after which the cyclohexane or benzene vapors were admitted, and then the cyclohexene vapors. The results of these experiments are summarized in Table 2. The first three experiments revealed that if the amount of hydrogen exceeds $9.8 \cdot 10^{16}$ molecules, then the hydrogenation of the cyclohexene predominates, while with smaller amounts of hydrogen the dehydrogenation predominates. From

Expt. Nos. 4 and 5 it follows that cyclohexane remains unchanged under these conditions and does not affect the extent of cyclohexene conversion: the ΔN_{H_2} are the same in Expt. Nos. 3 and 5. Benzene is not hydrogenated here (see Expt. No. 6), but it does sharply increase the ratio of the hydrogenation and dehydrogenation rates of cyclohexene.* This makes it possible to explain the analogous effect in Expt. No. 10 of Table 1 by the adsorption of the benzene formed in Expt. No. 9, on those portions of the film surface where the dehydrogenation of the cyclohexene takes place. Evacuation of the reaction products or specially admitted benzene leads to the usual ratio of the hydrogenation and dehydrogenation rates, as can be seen from Expt. Nos. 1-9 in Table 1 and from a comparison of the results of Expt. Nos. 2 and 3 with those of No. 8 in Table 2. In all of these experiments ΔN_{H_2} decreases steadily with increase in N_{H_2}.

TABLE 1. Change in the Amount of Hydrogen in the Vessel Containing the Film After the Admittance of $2.8 \cdot 10^{16}$ Molecules of Cyclohexene

Expt. No.	1	2	3	4	5	6	7	8	9	10
Before admission	0	0	2,7	6,3	8,0	7,9	37,4	33,3	30,8	29,8
After admission	2,7	2,7	1,6	1,1	−0,1	0	−4,1	−2,5	−1,0	−2,5

TABLE 2. Conversion of Cyclohexene on Platinum Film in the Presence of Cyclohexane and Benzene

Expt. No.	$N_{H_2} \cdot 10^{-16}$ before expt.	Vapor pressure, mm		$N_{C_6H_{10}} \cdot 10^{-16}$	$N_{H_2} \cdot 10^{-16}$ after expt.	$\Delta N_{H_2} \cdot 10^{-16}$	Expt. No.	$N_{H_2} \cdot 10^{-16}$ before expt.	Vapor pressure, mm		$N_{C_6H_{10}} \cdot 10^{-16}$	$N_{H_2} \cdot 10^{-16}$ after expt.	$\Delta N_{H_2} \cdot 10^{-16}$
		C_6H_{12}	C_6H_6						C_6H_{12}	C_6H_6			
1	7,1	—	—	2,8	7,3	0,2	5	16,4	$2,10^{-2}$	—	2,8	15,6	−0,8
2	9,8	—	—	2,8	9,8	0,0	6	15,6	—	$3,1 \cdot 10^{-2}$	—	15,6	0,0
3	17,2	—	—	2,8	16,4	−0,8	7	15,6	—	$3,1 \cdot 10^{-2}$	2,8	13,3	−2,3
4	16,4	$2,10^{-2}$	—	—	16,4	0,0	8	13,3	—	—	2,8	12,8	−0,5

If the proposed explanation is true, then with a continuous removal of the reaction products the amount of hydrogen liberated from the cyclohexene should be greater than that liberated in the above described experiments. To verify this we ran two experiments using one film, the same amounts of hydrogen in the adsorption vessel, and also the same rates and times of admitting the cyclohexene. In the first experiment, where the entire system was found at 20°, the maximum hydrogen pressure was $2 \cdot 10^{-3}$ mm; in the second experiment the outlet found around the adsorption vessel was cooled with liquid nitrogen. Together with the reaction products, a part of the admitted cyclohexene also condensed in the outlet, but despite this the hydrogen pressure exceeded $2 \cdot 10^{-2}$ mm and continued to grow. Consequently, if the benzene formed in the dehydrogenation of cyclohexene is continuously removed from the platinum film, then the dehydrogenation process actually dominates over the hydrogenation.

The above shows that both the dehydrogenation and hydrogenation of cyclohexene and 1,3-cyclohexadiene take place on platinum films at 20°. At low pressures the dehydrogenation predominates. The accumulation of hydrogen and benzene, which leads to a preferential blocking of the active dehydrogenation centers, results in the situation that the dehydrogenation rate decreases, and the hydrogenation rate increases. For this reason, with increase in the pressure of the unsaturated hydrocarbon the amount of hydrogen in the gas phase decreases, and the composition of the reaction products is always more accurately described by Eqs. (1) and (2), although they do not reflect the studied transformations. To determine whether a direct transfer of hydrogen takes place along with these transformations requires a special investigation.

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THE FORMATION OF COARSE MICROSCOPIC GROWTHS IN CRYSTALLINE POLYPROPYLENE

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Translated from Doklady Akademii Nauk SSSR, Vol. 139, No. 4, pp. 874-876, August, 1961
Original article submitted April 12, 1961

In most of the papers published up to now a study of the crystallization process of polymeric substances was made either in dilute solutions, or in thin films, where the dimetric character of the film could not affect the character of the structure formed. However, the greatest interest is obviously possessed by a study of the crystalline forms, arising directly in the block of the polymeric substance, which has great importance for the molding and processing of polymeric materials. Studies in this direction have been conducted mainly along the lines of an electron-microscope investigation of the fine structure of the surface of a fractured crystalline polymer [1-4], and it was only very recently that a statement appeared on the existence of secondary structures of microscopic size in the mass of the polymeric substance, which structures were brought out in the process of etching a cut of the block polymer with poor solvents [5, 6].

The present paper is devoted to a study of the microscopic structures of isotactic polypropylene, arising in the mass of the polymeric substance in the process of slow cooling from the melt. Polypropylene specimens with a molecular weight of about 100,000 were used in the study. The molten polymer was cooled slowly (at a rate of 0.07 deg/min) to the desired temperature, and then it was kept at this temperature for 6 hr. The material taken for study was the surface of a brittle fracture, obtained in the impact deformation of the specimen at the temperature of liquid nitrogen. The study was made using a type MIM-8M metallographic microscope.

As a result of the study we were the first to show that the process of crystallization in the condensed phase of the polymer can go up to the formation of very coarse (40-200 μ in diameter) spherically symmetrical structures of the spherulite type, exhibiting clearly defined boundary lines (Figs. 1 and 2). As a result, during the cooling of the molten polymeric mass the process of orderly rearrangement succeeds in reaching the stage of the formation of completely crystalline structures in a relatively short time. It is impossible to visualize this if the molten polymer is regarded as being a system composed of disorderly entangled chains. It is obvious that a certain preliminary orderliness in the arrangement of the molecular chains should exist even in the molten polymer, and only a completion of this orderliness, ending in the formation of the crystalline phase, is achieved during the cooling process.

The fact that such coarse spherulites are formed in the process of the crystallization of the polymer under conditions of high viscosity and, consequently, a low mobility of the chains is new evidence in support of the theory of the bundle structure of polymers, first proposed by V. A. Kargin, G. L. Slonimskii and A. I. Kitaigorodskii [7]. According to this theory, polymers in the crystalline and even in the amorphous state are regarded as being well ordered systems, built either from globules or from unfolded chains, collected in bundles [8]. The crystallization process begins with the crystallization of the bundle, while the formation of a crystalline structure is the last stage in the orderly rearrangement of the chains. The single crystals are the most complete crystalline form. However, most frequently the process of crystallization in polymers does not succeed in reaching the formation of the monocrystals, but instead stops at the formation of the less complete secondary structures of the spherulites. From the kinetic standpoint the formation of spherulites is the preferred one, for this process requires a minimum rebuilding of the poorly mobile structure of the crystalline polymer. On the basis of the present study it can be seen that crystallization in the condensed phase of the polymer can lead to the formation of very coarse spherulites.

However, it should be mentioned that in the crystallization of block polypropylene at various crystallization temperatures we were able to observe in many cases, together with the formation of large spherulitic structures, also the formation of very coarse (exceeding 200 μ) regularly shaped growths, not having the radially symmetrical shape of spherulites and in external appearance resembling the individual crystals (Fig. 3). The results of studying such structures will be the subject of later papers.

To determine the effect of the crystallization temperature on the structure of the formed spherulites we made a study of the crystallization of polypropylene in a wide temperature range. The following rules were derived from this study:

1. Depending on the crystallization temperature, changes are observed in the dimensions of the spherulites. Spherulites, the diameter of which reaches values of the order of 40-100 μ, are formed in the temperature range 130-140°. The spherulites, obtained at crystallization temperatures in the vicinity of 100°, range in diameter from 160 to 220 μ. As can be seen from Figs. 1b and 2, the spherulites exhibit well defined boundary lines.

2. The crystallization temperature also influences the structure of the spherulites. The spherulites obtained at temperatures above 100° have a lamellar structure. On going to temperatures below 100° the lamellar character of the structural elements of the spherulites changes to a fibrillar nature, clear up to the complete formation of spherulitic growths in the system of entangled fibrils.

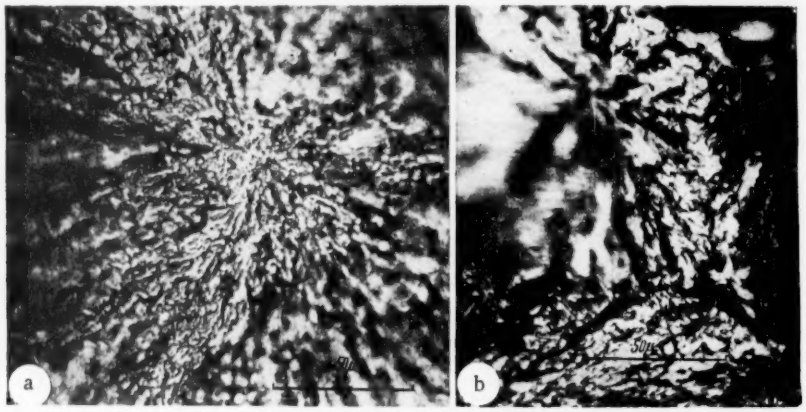

Fig. 1. Microphotograph of surface of fractured block polypropylene, allowed to crystallize by slow cooling (24 hr) of the melt from 180 to 100°.

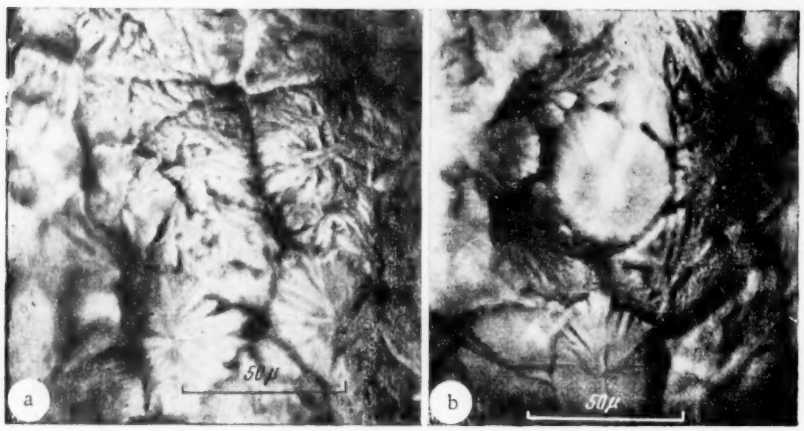

Fig. 2. Microstructure of surface of torn block polypropylene, allowed to crystallize by rapid cooling (2 hr) of the melt from 180 to 100° and subsequent holding at this temperature for 6 hr.

The crystalline structure of a polymeric substance obviously exerts an important influence on the character of the destruction of a polymeric material. In the case of a brittle fracture of block polypropylene, with coarse formations present, the destruction possibly takes place along the boundaries of the crystalline grains. If such is the

case, then increasing the size of the spherulites should be accompanied by a substantial increase in the brittleness of the material. As a matter of fact, polypropylene specimens, in which the spherulites reach a size of the order of 200 μ, decompose much more easily than do block polymers containing finer crystalline formations. But in many cases a destruction of the spherulite itself occurs during impact deformation and then the lamellar character of its structural elements appears.

As a result, it was shown by us that the process of the crystallization of isotactic polypropylene in the condensed phase can extend to the formation of very coarse spherulites and even single crystals, and that the size and character of the structural elements of the spherulites change with change in the crystallization temperature. Without doubt, such crystalline formations exert an important effect on the properties of a polymeric material.

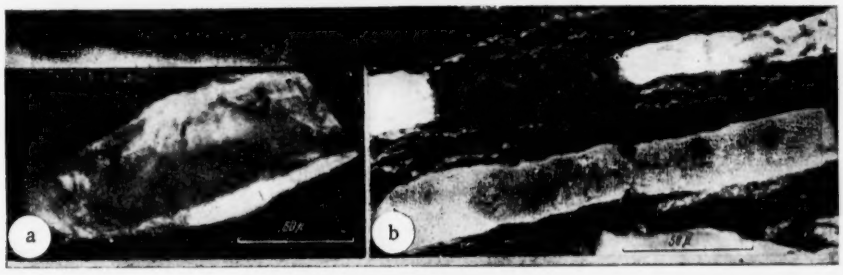

Fig. 3. Microstructure of surface fractured block polypropylene, obtained by chilling the melt in liquid nitrogen. Coarse formations resembling single crystals can be seen.

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REACTION OF ETHYLENIMINE WITH CARBONYL COMPOUNDS

R. G. Kostyanovskii

(Presented by Academician I. L. Knunyants, January 18, 1961)
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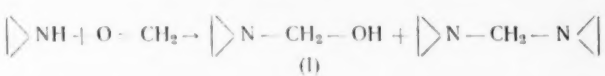
Original article submitted January 10, 1961

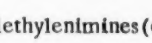
Based on the data of Doughty and co-workers [1], the idea arose in the literature that the reaction of ethylenimine with aldehydes and ketones under mild conditions yields oxazolidines.

In a previous paper we described the reaction of ethylenimine with formaldehyde [2]:

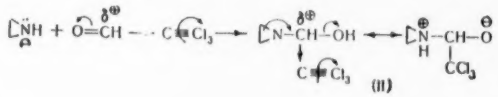


(I)

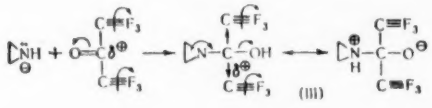
Despite the higher polarization of the carbonyl group in formaldehyde when compared with the carbonyl compounds studied in [1], we were unable to observe the formation of oxazolidine.

Simultaneously with the publication of our paper [2], Giller and Lidak reported that the products of the reaction of ethylenimine with aldehydes, described by Doughty as being oxazolidines, in their chemical and physicochemical properties correspond to the α-alkyl-N-methylolethylenimines (derivatives of zinimine I [3]):  where R is a postively induced substituent.

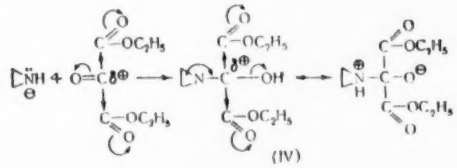
In the present study it was shown that this type of reaction can also be extended to carbonyl compounds containing strong negatively induced substituents (chloral, hexafluoroacetone, diethyl ester of mesoxalic acid), and, consequently, is a general reaction for all types of carbonyl compounds. The studied reactions can be depicted by the scheme:



(II)



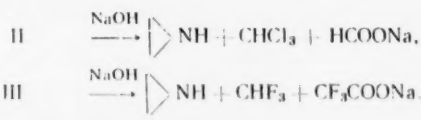
(III)



(IV)

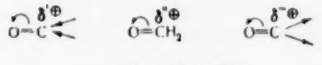
α-Trichloromethyl-N-methylolethylenimine (α-trichloromethylzinimine II), α,α-bis-trifluoromethyl-N-methylolethylenimine (α,α-bis-trifluoromethylzinimine III) and α,α-bis-carbethoxy-N-methylolethylenimine (α,α-bis-carbethoxyzinimine IV) are white crystalline compounds, readily subliming in vacuo. II on long storage or when heated turns yellow and decomposes with the liberation of chloroform and the formation of a viscous tar. The process is apparently due to the spontaneous haloform decomposition and polymerization of the formed N-formylethylenimine. III does not change on storage, while IV turns yellow and decomposes.

The structure of II and of III was shown by identifying the products of the haloform decomposition when the compounds were treated with caustic:



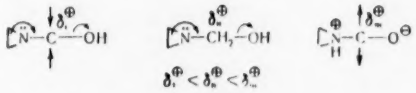
The structures of II, III and IV were also confirmed by the infrared spectra* (the figure), which show good agreement with the spectra for N-substituted ethylenimine derivatives [2-4]. In contrast to the earlier described methylol derivatives of ethylenimine, the spectra of II, III and IV have a broad band with a maximum at 2994 cm^{-1}, characteristic for the zwitter-ion. It is interesting to mention that the stability of the adducts of polyhalocarbonyl compounds with amines is greatly dependent on the basicity of the latter. Thus, with amines (K_a $10^{-3} - 10^{-4}$) the adducts are unstable and undergo spontaneous haloform decomposition [5-7]. With ammonia (K_a $1.79 - 2 \cdot 10^{-5}$) the adducts are stable (chloralammonia) and, finally, with aniline (K_a $5.3 \cdot 10^{-10}$) the perfluoroheptanone is completely unreactive under mild conditions [5], while hexafluoroacetone under drastic conditions gives cyclic rearrangement products of the hexafluoroisopropanol moiety [8]. Consequently, the stability of II and III can be explained by the optimum basicity of ethylenimine (K_a $0.81 - 1.0 \cdot 10^{-6}$). It is apparently for this reason that the adducts of hexafluoroacetone with secondary aliphatic amines, the basicity of which, despite the structural similarity of ethylenimine, is several orders of magnitude higher (dimethylamine, K_a $5.2 \cdot 10^{-4}$), are not reported in the literature.

The reaction rate of ethylenimine with carbonyl compounds steadily increases in the order:



$$\delta^{\oplus} < \delta'^{\oplus} < \delta''^{\oplus}$$

in harmony with the increased polarization of the carbonyl group. An interesting relationship is observed in the properties of the products of this reaction:



$$\delta_1^{\oplus} < \delta_2^{\oplus} < \delta_3^{\oplus}$$

The boiling point rises sharply when going from the first type of compounds to the second, while both groups of compounds are susceptible to methylation of the ethylenimino group, which is expressed in the formation of methylene-bis-ethylenimines [2, 9]. The third group of compounds are crystalline products that sublime readily, and whose saltlike character increases with increase in the electrophilicity of the substituents. The infrared spectra of the first and second groups of compounds contain the vibration bands of C—O and the O—H linkages of the hydroxyl group; the spectra of the third group of compounds contain a distinct zwitter-ion region, which testifies to the localization of the hydroxyl proton on the nitrogen of the amino group.

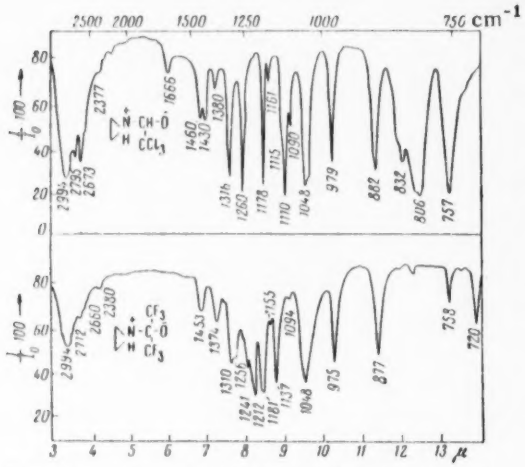
EXPERIMENTAL

α-Trichloromethyl-N-methylolethylenimine (II). A solution of 5.8 g (0.134 mole) of ethylenimine in 10 ml of absolute ether was added dropwise in 30 min to a solution of 19.8 g (0.134 mole) of chloral in 20 ml of absolute ether, cooled to 0°. The solvent was then removed, and the light-colored sirupy residue crystallized when 5 ml of absolute ether was added. We obtained 21.8 g of white crystals, yield 85.1%, b. p. 73-76° at 5-7 mm; after sublimation (50° at 5 mm), m.p. 83.5-84° (with sublimation).

(II) was also obtained by reacting chloral hydrate with ethylenimine in ether (refluxing for 1 hr). The product is soluble in ether, alcohol, benzene, chloroform, and dioxane; it is slightly soluble in water and insoluble in petroleum ether. It can be recrystallized from ether, dibutyl ether, or kerosine. Found mole wt. 198.8, 204.6; calculated 190.47.

*I wish to thank Yu. N. Sheinker for taking the spectra.

Found %: C 25.60, 25.61; H 3.36, 3.55; N 7.50, 7.57; Cl 55.71, 55.79. $C_4H_6ONCl_3$. Calculated %: C 25.22; H 3.18; N 7.35; Cl 55.84.



Infrared spectra of α-trichloromethyl-N-methyolethylenimine and α,α-bis-trifluoromethyl-N-methylolethylenimine.

α,α-Bis-trifluoromethyl-N-methylolethylenimine (III). A solution of 3.2 g of ethylenimine in 30 ml of absolute ether was added dropwise in 1 hr to a solution of 7 ml of hexafluoroacetone in 30 ml of absolute ether at −60°. Then the mixture was allowed to warm up to room temperature, refluxed for 5 min, and allowed to stand overnight at room temperature. After removal of the solvent we obtained 9.2 g of a white crystalline product, yield 59.3%. After sublimation (100° at 20 mm), m. p. 147-149.5°.

The product is soluble in ether, acetone, and dioxane; it is difficultly soluble in chloroform and insoluble in water, benzene or petroleum ether.

Found %: C 28.29, 28.35; H 2.22, 2.26; N 6.86, 6.93; F 53.74, 53.93. $C_5H_5ONF_6$. Calculated %: C 28.82; H 2.41; N 6.7; F 54.51.

α,α-Bis-carbethoxy-N-methylolethylenimine (IV). A solution of 9.85 g of diethyl mesoxalate in 50 ml of absolute ether was treated at 0° with a solution of 2.5 g of ethylenimine in 30 ml of absolute ether. The mixture was allowed to stand overnight with cooling; we obtained 9.9 g of coarse white tablets, yield 80.6%, m. p. 68-69° (from ether).

Found %: C 49.82, 49.98; H 7.10, 7.19; N 6.50, 6.55. $C_9H_{15}O_5N$. Calculated %: C 49.76; H 6.96; N 6.44.

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DISSOCIATION HEATS* OF KURNAKOV COMPOUNDS Ni_3Fe, Ni_3Mn, Ni_3Cr and Ni_3V

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A. A. Baikov Institute of Metallurgy, Academy of Sciences of the USSR

(Presented by Academician I. I. Chernyaev, March 13, 1961)
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In 1914 N. S. Kurnakov, on the example of the system copper–gold, was the first to establish the formation of metallic compounds from solid solutions [1]. Subsequent studies of metallic systems employing physicochemical analysis methods made it possible to uncover similar phenomena in many solid solutions of metals. In honor of their discoverer, these compounds formed from solid solutions, were named Kurnakov compounds [2]. However, in the literature, and mainly in the foreign literature [3, 4], the formation of compounds from solid solutions is frequently regarded as being a simple atomic rearrangement associated with an ordering of the structure in a homogeneous medium, without phase transformation.

The formation of metallic compounds of composition Ni_3Me from solid solutions occurs in the systems nickel–iron, nickel–manganese, and nickel–chromium. However, usually only a dotted line of the critical temperatures for the ordering of the solid solutions is given on the equilibrium diagrams of these systems in the region of 75% nickel [5].

Together with this, phase transformations with the formation of metallic compounds should be accompanied by a considerable change in the energy, and an independent region of the extension of these compounds, including the two-phase region, should exist on the diagram of state of the system.

Determination of the heats of the phase transformations of alloys of composition Ni_3Me in the systems nickel–iron, nickel–manganese and nickel–chromium, and a comparison of these values with the heats of formation of the compounds Ni_3V and Ni_3Ti could give additional information regarding the nature of the transformations in these systems.

A study was made in [6] of the effect of the disordering process on the temperature course of the heat capacity of the alloy Ni_3Fe, previously annealed for 500 hr in the temperature range from 490° to 370°. The value of the energy of disordering the alloy, found to be equal to 0.8 kcal/g-atom, was calculated by integration of the heat capacity in the temperature range from 325° to 625°. The data on the corresponding heats in the systems nickel–manganese, nickel–chromium and nickel–vanadium are not found in the literature. For the heat of formation of the metallic compound Ni_3Ti, which is formed from the melt during crystallization, it is possible to use the value proposed by Kubaschewski in [7].

In the present study the thermographic method, developed by L. G. Berg and V. Ya. Anosov [8], was used to determine the heats of the phase transformations in the systems nickel–iron, nickel–manganese, nickel–chromium, and nickel–vanadium. The method consists in comparing the areas of the peaks on the differential heating curve corresponding to the heat effects in the standard and the sample. In our work we used the split standard method [9]. We selected iron as the reference standard; the heat effects of the magnetic $\alpha \rightarrow \beta$ and polymorphous $\beta \rightarrow \gamma$ transformations of iron have been measured calorimetrically and tabulated [10]. Knowing the heat effects of these two transformations, the relative error of determination using the selected method can be established by calculating the value of one heat effect from the known value of the other and then comparing it with the tabulated value. As the calculations show, the discrepancy between the experimental value of the heat of the $\alpha \rightarrow \beta$ Fe-transformation and the tabulated is within 2-5%, i.e., within the limits of the accuracy of the method used.

Together with iron, nickel was used as a standard in determining the heat effects of the transformations in the alloys nickel–manganese, nickel–iron, and nickel–chromium. The areas of the heat effects were measured by the convenient and simple method of geometric integration using a lined transparent sheet divided into squares [11].

* The heat of transition of a compound into solid solution at the critical transition temperature is called the heat of dissociation.

It should be mentioned that the thermographic method of determining heat effects has been subjected to broad experimental verification on salt systems and natural-occurring compounds, but it has hardly been used for investigating metals and alloys. At the same time, such systems, due to the high heat conductivity and compactness of the material, are extremely convenient subjects for such a method of investigating the heats of reaction in the solid state.

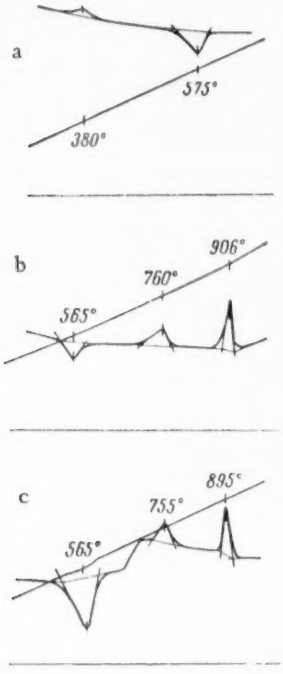

Fig. 1. Heating curves of the alloy Ni_3Fe: a) nickel standard; b) and c) iron standard.

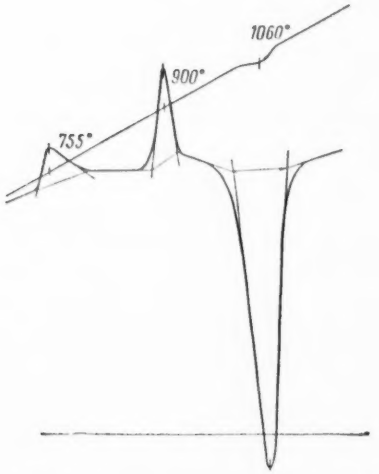

Fig. 3. Heating curve of alloy Ni_3V after annealing the alloy for 1400 hr at 950°.

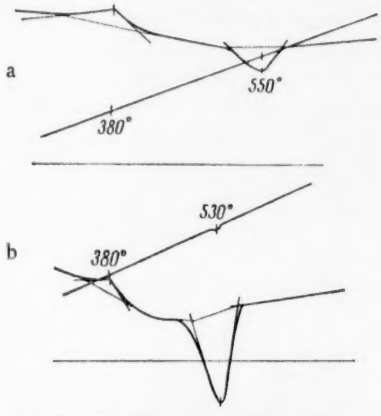

Fig. 2. Heating curve of the alloy Ni_3Mn: a) after annealing for 700 hr; b) after annealing for 1400 hr.

The Ni_3M3 alloys were prepared in an arc furnace in an argon atmosphere from electrolytic nickel, iron, manganese and chromium and carbothermal vanadium, the latter containing 99.8% vanadium. The alloys used in the investigation were selected on the basis of the chemical analysis and corresponded almost exactly with the stoichiometric composition Ni_3Me. The thermal treatment of the alloys consisted in a high-temperature homogenization annealing and prolonged annealing below the critical transition temperature: for Ni_3Fe, Ni_3Mn and Ni_3Cr at 450°, and for Ni_3V at 950°. Determination of the heat effects was made after 700, 1000 and 1400 hr of annealing, i.e., as a function of the time of bringing the alloys to the equilibrium state. The conditions used in recording the heating curves of all of the investigated alloys of composition Ni_3Me were maintained strictly constant, which facilitated a good reproducibility of the experimental results.

The heating curves of the alloy Ni_3Fe in pair with nickel and in pair with iron, after 700 hr of annealing, are shown in Fig. 1. These curves show substantial endothermic effects of the dissociation of the metallic compound Ni_3Fe formed as a result of the long annealing. The value of this heat effect ΔH, corresponding to the equilibrium state, was determined by comparison with nickel, as well as by comparison with iron, and is 1.97 kcal/g-atom. It is greater than the value proposed in [6] and can be attributed to the more uniform state of the alloy reached as a result of the thermal treatment employed in our work. Reproduction of the recording on

Compound	Chemical composition, wt.%		Critical temperature, °C (Kurnakov point)	Dissociation heat of compound, ΔH		Relative error of measurement, %
	theory	found		kcal/g-atom	cal/g	
Ni_3Fe	24,08	24,20	570	1,9±0,1	34±2	5
Ni_3Mn	23,77	23,40	540	2,40±0,09	41,5±1,6	3
Ni_3Cr	22,80	22,75	585	0,41±0,005	7,2±0,1	1,5
Ni_3V	22,44	22,60	1070	3,60±0,2	63,5±3,4	5
Ni_3Ti	—	—	1380	8,4	—	—

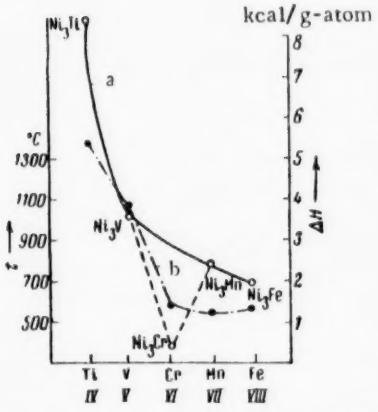

Fig. 4. Dependence of the heats (ΔH) and temperatures of dissociation of the compounds Ni_3Me on the position of Me in the periodic system: a) dissociation heats; b) dissociation temperatures.

several samples gave a deviation not exceeding 5%. The dissociation temperature of the compound is 570°.

The heating curves of the alloy Ni_3Mn, after annealing for 700 and 1400 hr, are shown in Fig. 2. As can be seen from the thermograms, increasing the time of annealing to 1400 hr gives a substantial increase in the magnitude of the heat effect. A further increase in the annealing time does not change the value of the heat effect (the area of the peak on the differential curve). For the equilibrium state this value is equal to 2.40 kcal/g-atom. The dissociation temperature of the compound Ni_3Mn is 540°. The heating curves of the alloy Ni_3Cr also show distinct endothermic effects of phase transformation. Increasing the time of annealing from 700 to 1400 hr gives only a two-fold increase in the value of the heat effect, and a further continuation of the annealing at the same temperature does not change this value.

Annealing for 2000 hr at 400 and at 500° does not give an increase in the heat effect, and instead the heat effect is decreased.

The highest value of ΔH, reached after annealing for 1400 hr at 450°, is 0.41 kcal/g-atom, i.e., it is considerably lower than the ΔH values for Ni_3Fe, Ni_3Mn, and Ni_3V. It is possible to assume that the process for the formation of the compound goes with exceeding slowness and consequently the equilibrium state of the alloy was practically not reached. The question of whether the compound Ni_3Cr requires further study in connection with the low value of its heat of formation (dissociation) becomes all the more urgent since some authors [12] postulate the presence of the K-state in the annealed alloy, while others postulate that the compound Ni_2Cr is present instead of Ni_3Cr [3].

The value of the heat effect of the dissociation of compound Ni_3V, corresponding to the equilibrium state, which is reached after annealing the alloy at 950° for 1400 hr is 3.60 kcal/g-atom (Fig. 3). The dissociation temperature is 1070°.

The data on the chemical composition of the investigated compounds, their temperatures of formation and their heats of dissociation are summarized in the table.

Attention should be given to the large value of the dissociation heats, constituting a whole number of large calories per gram-atom. Only the compound Ni_3Cr is an exception in this respect. It is obvious that the strength of the chemical bond in the alloys annealed for a long time has a different nature than in solid solutions, and that the processes of orderly arrangement in the investigated alloys are linked with the formation of strong and stable metallic compounds. They should have independent regions of existence on the diagram of state of the system, and, as phase transformations of the 1st order, also two-phase regions. A classic example of a similar transformation is found in the system copper–gold for the composition Cu_3Au [1, 3].

The dependence of the heats and temperatures of dissociation of the compounds Ni_3Fe, Ni_3Mn, Ni_3Cr, Ni_3V and Ni_3Ti on the position of the metals in the periodic system of the elements is shown in Fig. 4. From a comparison of this data it can be concluded that the dissociation heats for all of the compounds are commensurate, and that with the exception of the ΔH of Ni_3Cr, they increase with increase in the distance between the position of the metal present in the compound and that of nickel in the periodic system. As a result, for the investigated series of compounds a definite relationship is observed between the properties of the chemical compounds and the position of the components

in the periodic system. The strength of the chemical bond in the compounds Ni_3Fe, Ni_3Mn, Ni_3V and Ni_3Ti is apparently also determined by the heats of formation (dissociation); it increases with increase in the difference in the chemical properties of the reacting metals, i.e., it is linked with the position of the reacting elements in the periodic system.

An increase in the strength of the chemical bond in the series of compounds Ni_3Fe, Ni_3Mn, Ni_3Cr (?), Ni_3V and Ni_3Ti should find reflection in the mechanical strength of these compounds, which requires additional study.

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THE POLYMERIC NATURE OF 5/6 BASIC ALUMINUM CHLORIDE AND THE POSSIBILITY OF THE EXISTENCE OF ALUMINUM OXYCHLORIDES OF HIGHER BASICITY

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In a number of investigations [1-3] it was shown that the soluble basic salts of aluminum tend to form a high molecular weight complexes. It may be assumed that the tendency to form such products is most clearly manifested in highly basic systems. From this standpoint it seems of interest to study some of the physical properties of 5/6 basic aluminum chloride, $Al_2(OH)_5Cl$ [4].

In the present paper our goal was to determine the possibility of forming polymeric products from 5/6 basic aluminum chloride. Polymeric substances are characterized by a number of specific properties, of which the more important ones are: 1) a high viscosity of the solutions; 2) the ability to swell in solvents and the formation of systems lying intermediate between solid and liquid; 3) the ability to form fibers and films (anisotropy of the properties).

It is obvious that if 5/6 basic aluminum chloride is capable of forming polymers, then these products should possess the above indicated complex of physical properties.

The compounds used in our study were prepared by dissolving either aluminum metal or pure aluminum hydroxide in hydrochloric acid. As is known, both of these methods permit obtaining products with a high ionic weight [2].

With increase in the concentration of the 5/6 basic chloride in the system $Al_2(OH)_5Cl-H_2O$, the appearance of the system changes in the following manner:

Al_2O_3 concn., %	Appearance of system
0–20	Solution
25–28	Gelatinous
30–40	Glassy
>40	Powdery

The transition along the series solution–powder is completely reversible. The addition of small amounts of water to the powder causes it to swell with the formation of a gel. With increase in the dilution, the oxychloride changes to a true solution. We will mention that swelling is typical for polymers when a solvent is added. The gelatinous product is quite thixotropic, which is characteristic for polymers, the macromolecules of which are somwhat branched.

Some of the properties of solutions of 5/6 basic aluminum chloride had been investigated earlier [5]. It was shown that in the investigated concentration range (0 – 200 g/liter Al_2O_3 at 20° and 0 – 300 g/liter Al_2O_3 at 75°) the change in the density of the solutions is trictly linear. As is known [6], $Al_2(OH)_5Cl$ is a substance with practically unlimited solubility. In the investigated concentration range the density changed in exactly the same manner as in the case of aqueous solutions of electrolytes, where any qualitative changes (for example, the formation of hydrates) fail to occur with increase in the concentration [7].

However, the character of the change in the viscosity of the $Al_2(OH)_5Cl$ solution at 20 and 75° differed sharply from the curves for the change in the viscosity of aqueous solutions of electrolytes with change in the concentration [5, 7]. These curves proved to be quite similar to the graphs plotted for such a typical polymeric substance as polyisobutylene when dissolved in various solvents (heptane, hexane, toluene). This is supported by Fig. 1, where the obtained data on the change in the viscosity with change in the concentration [5] are interpreted for the reduced

viscosity. As can be seen from the graph, the intrinsic viscosity of the 5/6 basic chloride solution at 20° is quite different from zero and is equal to 0.06. As a result, in a number of their properties the investigated 5/6 basic aluminum chloride solutions are identical with polymer solutions.

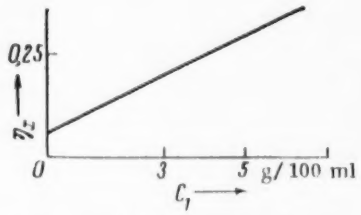

Fig. 1. Reduced viscosity of solutions of 5/6 basic aluminum chloride at 20°C.

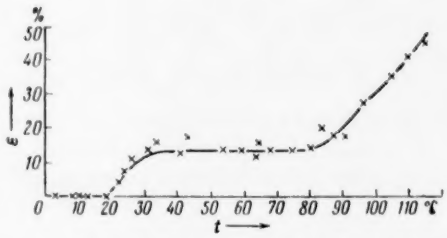

Fig. 2. Thermomechanical curve of the glassy 5/6 basic aluminum chloride specimen.

A study of the dependence of the mechanical properties of the condensed (glassy) 5/6 basic aluminum chloride on the temperature was of considerable interest. Testing of the specimen, prepared as tablets 8 mm in diameter and 4 mm high, was done using a dynamometric balance with a compression load of 1.59 kg/sq cm and a load time of 10 sec. The results are plotted in Fig. 2, from which it can be seen that the 5/6 basic chloride goes through three physical states when the temperature is raised: at 25° it goes from a glassy state to a highly elastic state (inherent only to polymeric substances), while at 90° it changes to a state of viscous flow.

During the course of the experiments it was also repeatedly observed that 5/6 basic aluminum chloride tends to form films. This anisotropy in the properties of the substance has been utilized in a number of studies. Thus, recently, papers have appeared on the use of 5/6 basic aluminum chloride as a binder in fire-resistant cements [8] (concentrated $Al_2(OH)_5Cl$ solutions have good adhesive properties) and on obtaining fibrous boehmite from a solution of the basic chloride, which has found various utility [9].

As a result, based on its aggregate properties, 5/6 basic aluminum chloride may be considered to be a substance that is capable of forming polymeric products.

The existence of some basic compound in the solution is proved by the presence of a corresponding inflection on the potentiometric titration curve. However, the polymerization of less basic compounds can distort the shape of the potentiometric titration curve. Klenert and Denk [12] observed that the amount of caustic that had to be added to a solution of the basic chloride to achieve a jump in the potential [for titration up to $Al(OH)_3$] changed in a complex manner during the aging of the solution (see Fig. 3).

Attempting to explain this phenomenon, the authors postulated that other reactions take place parallel with the hydrolysis, for example, for the solution of composition $Al(OH)_2Cl$.

The concept that 5/6 basic aluminum chloride has a polymeric nature makes it possible to explain certain experimental facts associated with the question of whether it is possible for the higher basic chlorides [i.e., intermediate in composition between $Al_2(OH)_5Cl$ and $Al(OH)_3$)] to exist as individual compounds. A number of papers have appeared recently on the discovery of higher aluminum oxychlorides. Denk and co-workers [11, 12] and Tanabe [13] have reported the 8/9 basic chloride $Al_3(OH)_8Cl$ and the 11/12 basic chloride $Al_4(OH)_{11}Cl$.

$$Al(OH)_2Cl + Al(OH)_3 = Al_2(OH)_5Cl, \quad (1)$$

$$3Al(OH)_2Cl = 2Al(OH)_3 + AlCl_3, \quad (2)$$

in which connection the first reaction favors a decrease in the alkali consumption, while the second reaction favors an increase; increasing the temperature favors the progress of both reaction (2) and the hydrolysis reaction:

$$Al(OH)_2Cl + HOH = Al(OH)_3 + HCl. \quad (3)$$

The unconvincing nature of such an explanation is obvious. First, even if all of the presented reactions take place, this in no way reflects on the hydroxyl-ion balance in the system. Second, it is known that 5/6 basic aluminum chloride is titrated quite easily with alkali to $Al(OH)_3$ [6]. Consequently, if the matter consisted only in the processes examined by the authors, then the amount of caustic solution, added up to the "jump in the potential" on the titration curve, should remain constant during the course of aging.

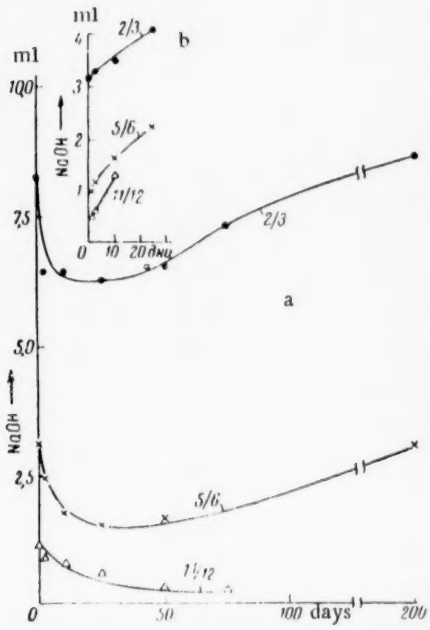

Fig. 3. Change in the amount of 0.1 N NaOH solution, added up to the points of reaching a "jump in the potential," during the aging of basic aluminum chloride solutions of variable basicity (based on the data given in [12]) at t = 20° (a) and 60° (b).

The gist of the observed phenomenon consists in the fact that a part of the aluminum-containing basic cations are "masked" during the aging process and consequently are not titrated by the alkali. It is quite possible that this is directly related with the formation of high-molecular compounds (polymers) during the aging of the 5/6 basic chloride, in which only a part of the aluminum can be neutralized (at the given rate of titration with alkali). Other changes in the system (aging of the aluminum hydroxide, hydrolysis of the 5/6 basic chloride and of the high-molecular product itself) will lead to the opposite result (an increase in the amount of alkali consumed to reach the "jump in the potential"). Obviously, heating facilitates hydrolysis more than it does polymerization, which causes a qualitative change in the character of the phenomenon with elevation of the temperature.

It is possible that this (a "masking" of a portion of the cations of the basic salt inside the macromolecule) also explains the appearance of the inflections on the potentiometric titration curves in the range of basicities OH/Al = 2.5–3. Actually, the titration of that portion of the aluminum-containing cations found inside the macromolecule should proceed at a higher hydroxyl-ion concentration than the titration of these same cations, found in the free state in the solution. For this reason, in the titration of the "masked" cations, additional inflections shifted toward higher values of the pH of the medium and the basicity of the solution, should appear on the potentiometric curve. Even greater difficulties are encountered in the titration of polymerized 5/6 basic aluminum chloride with sulfate-ion to yield the 5/6 basic aluminum sulfate as a precipitate, for example:

$$2Al_2(OH)_5Cl + Na_2SO_4 = (Al_2(OH)_5)_2SO_4 + 2\,NaCl.$$

It was shown by Denk [10] that the precipitate begins to form only when the amount of sulfate-ion in the solution is vastly in excess of the stoichiometric amount. Although this reaction undoubtedly has an ionic character, still even with a large excess of sulfate-ion the formation of the precipitate begins only after several hours (or days). Our experiments revealed that if conventional rates of titration are employed, a cloudiness of the 5/6 basic chloride solution begins only after the amount of added sulfate-ion is $4 \cdot 10^7$ greater than the amount needed to reach the solubility product of 5/6 basic aluminum sulfate.

It is obvious that the difficulties, encountered in the titration of the polymeric basic aluminum chloride with OH'-ions, should become even greater in the case of titration with SO_4"-ions in view of their lower mobility and the change in the order of the reaction.

As a result, highly basic aluminum chlorides (with an OH/Al basicity exceeding 2.5) can be regarded as being polymerized varieties of the 5/6 basic chloride $Al_2(OH)_5Cl$, and not as individual compounds.

Certain other experimental data also testify in support of the hypothesis expressed here. In particular, when excess aluminum metal is dissolved in hydrochloric acid the solution strives to attain the composition of the 5/6 basic chloride as a limit; solutions with an Al/Cl ratio exceeding 2 are not formed here [10]. When the amount of dissolved aluminum exceeds this ratio, the character of the system changes: the solution changes from a true to a colloidal solution [10, 14].

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PROPERTIES OF PHENYLFERROCENE

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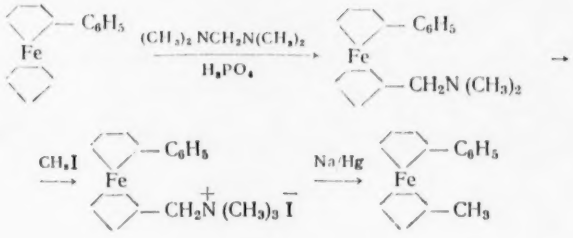
An alkyl group attached to the ferrocene ring facilitates subsequent electrophilic substitution, in which connection the cyclopentadienyl ring to which it is attached shows the stronger activation [1-4]. With respect to the ferrocenyl radical the phenyl group functions as an electron-acceptor, as we had first shown by comparing the basicity constant of p-ferrocenylalanine and the ionization constant of p-ferrocenylphenol with the constants of the corresponding benzene derivatives [5].

The data of Rosenblum [6] on the acylation of phenylferrocene confirm our results: the phenyl group, similar to other electron-acceptor substituents, exerts a deactivating influence on the electrophilic replacement of the hydrogens in the ferrocene ring.

In the present paper we studied the aminomethylation, sulfonation and nitration of phenylferrocene, and we also ran the competing (with ferrocene) acetylation of phenylferrocene. The aminomethylation of phenylferrocene was run using tetramethyldiaminomethane in the presence of phosphoric acid. Here we obtained (N,N-dimethylaminomethyl)phenylferrocene. The infrared spectrum of the crude product contained absorption bands in the vicinity of 1000 and 1100 cm^{-1}, but the intensity of the bands was weak. Apparently, the homocyclic isomer is formed in small amount. (N,N-Dimethylaminomethyl)phenylferrocene was converted to the methiodide and was reduced with sodium amalgam to methylphenylferrocene. The heterocyclic methylphenylferrocene was isolated from the reaction products in 70% yield, based on the aminomethylated phenylferrocene. This serves as evidence that the heterocyclic



isomer was the main component in the original mixture of(N,N-dimethylaminomethyl) phenylferrocenes and,consequently, the aminomethylation of phenylferrocene goes predominantly in the free cyclopentadienyl ring.

The sulfonation of phenylferrocene with dioxane-sulfur trioxide under the conditions used to obtain ferrocenemonosulfonic acid gave us 1,1'-phenylferrocenesulfonic acid. The acid was isolated

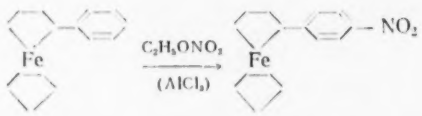
$$C_6H_5C_5H_4FeC_5H_5 \xrightarrow{\text{Dioxane-}SO_3} C_6H_5C_5H_4FeC_5H_4SO_3H$$

as the lead salt. The formation of the heterocyclic sulfonic acid also testifies to the lesser reactivity of the cyclopentadienyl ring attached to the phenyl group.

The deactivating influence of the phenyl group on the ferrocene ring is clearly manifested in the Friedel-Crafts reaction. Thus, the acylation of a mixture of phenylferrocene and ferrocene with acetyl chloride in the presence of aluminum chloride (all of the components were taken in a 1:1:1:1 molar ratio) gave acetylferrocene in 25% of the theoretical yield, while the yield of mixed acetylphenylferrocenes was only 5%, in which connection

64% of the phenylferrocene and 30% of the ferrocene were recovered unchanged. Consequently, ferrocene is acetylated much more easily than phenylferrocene.

To nitrate phenylferrocene we used ethyl nitrate in carbon disulfide medium, in the presence of $AlCl_3$, and obtained p-nitrophenylferrocene in 13% of the theoretical yield. It should be



mentioned that the main portion of the p-nitrophenylferrocene and a part of the unreacted phenylferrocene are isolated in the unoxidized form (and not in the form of the cation). It is obvious that the nitration reaction goes with phenylferrocene itself, and not with its cation. Here the attention is attracted to the retention of the ferrocenyl ring under these conditions, probably because of the somewhat lower ability to oxidize to the cation when compared to ferrocene. Ferrocene itself cannot be nitrated under these conditions.

Our attempts to nitrate ferrocene with various reagents, including nitronium borofluoride, proved unsuccessful. In all cases the ferrocene was oxidized to the cation, which is inert in electrophilic substitution reactions [7].

EXPERIMENTAL

Aminomethylation of phenylferrocene. To a mixture of 70 ml of glacial acetic acid and 4 g of H_3PO_4 (d 1.735), cooled to 10°, was gradually added 2.25 g (0.019 mole) of tetramethyldiaminomethane, and then 4 g (0.015 mole) of phenylferrocene. The reaction mass was stirred in a nitrogen stream for an hour at room temperature and for 10 hr at 110-115°, after which it was diluted with an equal volume of water, and the unreacted phenylferrocene (1.5 g) was extracted with benzene. The acid solution was treated with 40% NaOH solution and the (N,N-dimethylaminomethyl)-phenylferrocene was extracted with ether. After distilling off the ether we obtained 2.6 g of the aminomethylated phenylferrocene as a viscous, dark, reddish-brown oil. Yield 54% of theory, based on the phenylferrocene taken for reaction, and 86% based on the reacted phenylferrocene.

The (N,N-dimethylaminomethyl)phenylferrocene was vacuum-distilled. B. p. 150-160°/3 mm; $n^{20}D$ 1.6315.

Found %: C 72.09, 72.05; H 6.85, 6.87; N 4.83, 4.85. $C_{19}H_{21}NFe$. Calculated %: C 71.48; H 6.63; N 4.39.

The infrared spectrum of the obtained (N,N-dimethylaminomethyl)phenylferrocene contained weak absorption bands in the vicinity of 1000 and 1100 cm^{-1}, thus indicating that a mixture of the hetero- and homocyclic isomers was formed.*

(N,N-Dimethylaminomethyl)phenylferrocene methiodide was obtained by adding CH_3I to a solution of 3.2 g of the aminomethylated phenylferrocene in absolute CH_3OH (or in benzene), and after standing for 15 min the compound was precipitated by the addition of a large volume of dry ether. We obtained 4.3 g (nearly quantitative yield) of the methiodide as yellow crystals. M. p. 70-75° (decompn.).

Found %: C 51.77; H 5.40; Fe 12.50; N 2.87. $C_{20}H_{24}NIFe$. Calculated %: C 52.09; H 5.25; Fe 12.12; N 3.04.

The infrared spectrum of the methiodide, obtained from distilled (N,N-dimethylaminomethyl)phenylferrocene, did not show absorption in the vicinity of 1000 and 1100 cm^{-1}, which indicated that the substituting groups are found in different cyclopentadienyl rings.

1,1'-Methylphenylferrocene. A water solution of 4.3 g (0.0093 mole) of (N,N-dimethylaminomethyl)phenylferrocene methiodide** was added to the sodium amalgam obtained from 24 g of sodium and 24 ml of mercury. The mixture was heated at 80-90° for 4 hr. The methylphenylferrocene was extracted with petroleum ether and was purified by chromatographing on Al_2O_3, after which it was recrystallized from petroleum ether, and then from ethyl alcohol. Yield 1.8 g (71% of theory). M. p. 88.5-89.5°.

Found %: C 73.69, 73.63; H 6.00, 5.92; Fe 19.86, 20.12. $C_{12}H_{14}Fe$. Calculated %: C 73.93; H 5.83; Fe 20.22.

The mixed melting point with the 1,1'-methylphenylferrocene, obtained by us earlier [8] by the arylation of methylferrocene, was not depressed. The infrared spectra of both products were identical, and absorption in the

*The distilled product shows a much weaker absorption in this region than the undistilled.

**Obtained from the undistilled aminomethylated phenylferrocene.

vicinity of 1000 and 1100 cm^{-1} was absent. Using the infrared spectrum, it was shown that the free cyclopentadienyl ring exists only in the substance isolated from the mother liquors.

Sulfonation of phenylferrocene. With ice cooling, 10 g (0.060 mole) of freshly prepared dioxane-sulfur trioxide was added to a solution of 10 g (0.038 mole) of phenylferrocene in 100 ml of dichloroethane. After an hour the cooling was removed and the reaction mixture was allowed to stand for a day. Then the sulfonic acids were extracted with water.

The addition of lead carbonate to a water solution of the phenylferrocenesulfonic acid gave the lead salt, which crystallized as the tetrahydrate.

Found %: C 39.99, 39.68; H 3.97, 3.75. $C_{32}H_{34}O_{10}S_2Fe_2Pb$. Calculated %: C 39.96; H 3.67.

The infrared spectrum of the lead salt failed to show absorption in the vicinity of 1000 and 1100 cm^{-1}, and consequently the phenyl and the sulfonic groups are found in different cyclopentadienyl rings.

Unreacted phenylferrocene could not be detected in the reaction products.

Competing acetylation of ferrocene and phenylferrocene. A solution of 1.4 ml (0.02 mole) of acetyl chloride and 2.66 g (0.02 mole) of $AlCl_3$ in 10 ml of absolute ether was added in 20 min, with stirring, to a solution of 3.72 g (0.02 mole) of ferrocene and 5.42 g (0.02 mole) of phenylferrocene in 100 ml of CS_2. The stirring was continued for 45 min at room temperature and for 30 min with heating on the water bath. The reaction was conducted in a stream of pure nitrogen.

The cooled reaction mixture was poured over ice (300 g), containing 2 ml of concd. HCl. The water layer was separated, reduced with Na_2SO_3, and extracted with ether. The ether extracts were combined with the carbon disulfide layer, washed with 2 N NaOH and then with water, and dried over Na_2SO_4. The residue from the removal of the solvent in vacuo was dissolved in a 1:1 mixture of petroleum ether and benzene, and the solution was chromatographed on Al_2O_3. The ferrocene and phenylferrocene were eluted with petroleum ether, while a 1:1 mixture of petroleum ether and benzene was used to elute the acetylferrocene and acetylated phenylferrocenes. We isolated 1.1 g (30% of the amount taken) of ferrocene, m. p. and mixed m. p. 173-174°, 3.35 g (64%) of phenylferrocene, m. p. and mixed m. p. 109-110°, 1.15 g (25% yield) acetylferrocene, m. p. and mixed m. p. 83-84°, and 0.3 g (5%) of mixed acetylphenylferrocenes, m. p. 69-73°.

Found %: C 71.40, 71.57; H 5.50, 5.40; Fe 17.96, 18.18. $C_{18}H_{16}OFe$. Calculated %: C 71.07; H 5.30; Fe 18.36.

The infrared spectrum of the mixed acetylphenylferrocenes showed weak absorption at 1106 and 1002 cm^{-1}.

Repeated fractional crystallization of the mixed acetylphenylferrocenes from a 2:1 mixture of petroleum ether and ether gave the heterocyclic acetylphenylferrocene. M. p. 88.5-89.5°. Literature data [6]: m. p. 92.5-93.5°. The infrared spectrum fails to show frequencies in the 1000 and 1100 cm^{-1} regions.

Found %: C 71.31, 71.30; H 5.43, 6.51; Fe 18.20, 18.06. $C_{18}H_{10}OFe$. Calculated %: C 71.07; H 5.30; Fe 18.36.

Nitration of phenylferrocene. With stirring, a solution of 1 ml (0.1 mole) of ethyl nitrate in 25 ml of CS_2 was added in 10 min to a mixture of 2.62 g (0.01 mole) of phenylferrocene and 13.5 g (0.1 mole) of $AlCl_3$ in 50 ml of CS_2. This resulted in the formation of a dark precipitate, while the carbon disulfide became lighter in color. The carbon disulfide was decanted, and the residue was treated with 2 N HCl. The precipitate was filtered, washed with water, dried, and then extracted with ether until the extracts were colorless. The ether was removed by distillation; the residue was dissolved in petroleum ether and chromatographed on Al_2O_3. We isolated (petroleum ether was used for the elution) 0.1 g of starting phenylferrocene, m. p. and mixed m. p. 109-110°, and 0.35 g of p-nitrophenylferrocene, m. p. 167-168°; the mixed melting point with the p-nitrophenylferrocene, obtained by us earlier [9] by the arylation of ferrocene, was not depressed.

The hydrochloric acid solution was reduced with $SnCl_2$ (50 g). The obtained brown precipitate was filtered, washed with water, dried, and extracted with petroleum ether. The solution was chromatographed on Al_2O_3. We obtained an additional 0.15 g of phenylferrocene, m. p. 109-110°, and 0.05 g of p-nitrophenylferrocene, m. p. 167-168°.

In all we isolated 0.25 g (9.5% of the amount taken) of phenylferrocene and 0.40 g of p-nitrophenylferrocene; yield 13.0% of theory, based on the amount of phenylferrocene taken for reaction, and 14.2%, based on the reacted phenylferrocene.

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STUDY OF THE SYSTEM KF–ZrF_4

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Original article submitted March 18, 1961

Zirconium fluoride forms complex double salts with the alkali metal fluorides. Thus, in the system NaF–ZrF_4, studied by Barton and co-workers [1], were found the two incongruently melting compounds Na_3ZrF_7 and $Na_7Zr_6F_{31}$, the three compounds $Na_5Zr_2F_{13}$, Na_2ZrF_6 and $Na_3Zr_4F_{19}$, melting incongruently, and one compound – $Na_3Zr_2F_{11}$, existing only in the solid state.

According to the literature data, KF and ZrF_4 form the compounds: K_3ZrF_7, K_2ZrF_6 and $KZrF_5$. The fusion diagram of the system KF–ZrF_4 (up to 65% ZrF_4) was studied in [2, 3], apparently by the visual-polythermal method, since in [2] the phase fields below the solidus line are not shown on the diagram of this system. Also, nothing is said in [3] regarding the solid state transformations in this system.

In the present paper we made a differential thermal analysis and an x-ray phase study of the system KF–ZrF_4. According to the data in [4], zirconium fluoride undergoes polymorphous transformation at 405 ± 5°. Schulze [5] determined the parameters of the low-temperature monoclinic modification of ZrF_4: a = 9.46 A; b = 9.87 A; c = 7.64 A; β = 94°30'. According to the data of Barton [1], ZrF_4 melts at 912°. Sense and co-workers [6] determined the dependence of the vapor pressure of ZrF_4 on the temperature; according to their data the sublimation temperature of ZrF_4 is 903°.

Starting substances. For studying the indicated system we obtained potassium fluoride by the dehydration of $KF \cdot 2H_2O$, while the zirconium fluoride was prepared from $(NH_4)_3ZrF_7$ by distilling off ammonium fluoride in a CO_2 stream. The $(NH_4)_3ZrF_7$ was synthesized by the procedure given in [7].

To prepare the alloys, containing less than 33.3% ZrF_4, we used the potassium fluoride and the K_2ZrF_6 that we had on hand. The alloys, containing more than 33.3% ZrF_4, were prepared by fusing the calculated amounts of K_2ZrF_6 and $(NH_4)_3ZrF_7$ in a CO_2 stream. Alloys containing more than 75% ZrF_4 were not studied because of the volatility of ZrF_4. The results of analyzing the starting compounds and the obtained alloys for potassium, zirconium and fluorine showed good aggrement with the calculated values. The determination errors did not exceed 0.2-0.25%.

Thermal and x-ray phase analysis of the system KF–ZrF_4. An N. S. Kurnakov pyrometer, equipped with a Pt–PtRh thermocouple, was used to make the differential thermal analysis. Aluminum oxide served as the standard. The alloy samples taken for thermal analysis weighed 0.5 g. For the alloys, containing up to 33.3% ZrF_4, both the cooling and the heating curves were recorded. For the alloys containing more than 33.3% ZrF_4 only the cooling curves were recorded, since when the alloys were heated slowly their composition changed considerably. In order to reduce ZrF_4 losses, the alloys were introduced into the furnace at a temperature somewhat above the melting point of the alloy, and then after several minutes the furnace was turned off and the cooling curve was recorded. The temperatures were read at the start of the effect on the differential curve.

For the x-ray study the alloys were ground and then deposited on a Pyrex antenna using cellulose nitrate lacquer. The potassium fluoride and the alloys with a high KF content were photographed in sealed capillaries made of Pyrex glass. The x-ray patterns were photographed in RKD-57 cameras using Fe-radiation.

In view of the fact that a number of effects were found on the heating curves of K_2ZrF_6, associated with its transformations, we took the x-ray pattern of K_2ZrF_6 at 260 and 340° in a "Unicam" camera [8], using a BSVLT tube and a copper anode. It was impossible to photograph the x-ray pattern at a higher temperature because of the reaction of K_2ZrF_6 with quartz.*

*When the present work had been completed, a paper [9] appeared in the literature on the thermal stability and polymorphism of K_2ZrF_6.

The diagram of state of the system $KF-ZrF_4$, constructed by us on the basis of the thermal and x-ray phase analysis data, is shown in Figs. 1 and 2.

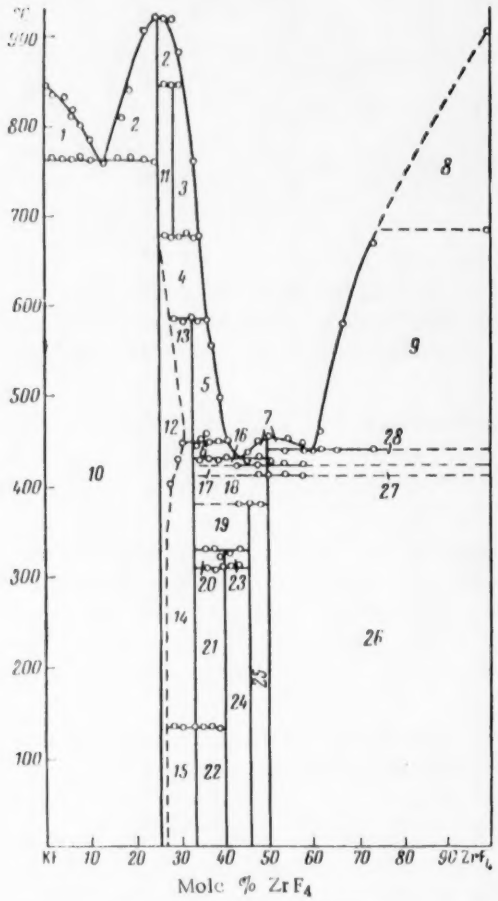

Fig. 1. System $KF-ZrF_4$. Phase fields: 1) KF + liquid; 2) K_3ZrF_7 + liquid; 3) $K_5Zr_2F_{13}$ + liquid; 4) solid solution + liquid; 5) δ-K_2ZrF_6 + liquid; 6) γ-K_2ZrF_6 + liquid; 7) γ-$KZrF_5$ + liquid; 8) β-ZrF_4 + + liquid; 9) α-ZrF_4 + liquid; 10) KF + K_3ZrF_7; 11) K_3ZrF_7 + $K_5Zr_2F_{13}$; 12) solid solution; 13) solid solution + δ-K_2ZrF_6; 14) solid solution + γ-K_2ZrF_6; 15) solid solution + α-K_2ZrF_6; 16) γ-K_2ZrF_6 + γ-$KZrF_5$; 17) γ-K_2ZrF_6 + β-$KZrF_5$; 18) γ-K_2ZrF_6 + α-$KZrF_5$; 19) γ-K_2ZrF_6 + $K_7Zr_6F_{31}$; 20) γ-K_2ZrF_6 + β-$K_3Zr_2F_{11}$; 21) γ-K_2ZrF_6 + α-$K_3Zr_2F_{11}$; 22) α-K_2ZrF_6 + α-$K_3Zr_2F_{11}$; 23) β-$K_3Zr_2F_{11}$ + $K_7Zr_6F_{31}$; 24) α-$K_3Zr_2F_{11}$ + + $K_7Zr_6F_{31}$; 25) α-$KZrF_5$ + $K_7Zr_6F_{31}$; 26) α-$KZrF_5$ + + α-ZrF_4; 27) β-$KZrF_5$ + α-ZrF_4; 28) γ-$KZrF_5$ + + α-ZrF_4.

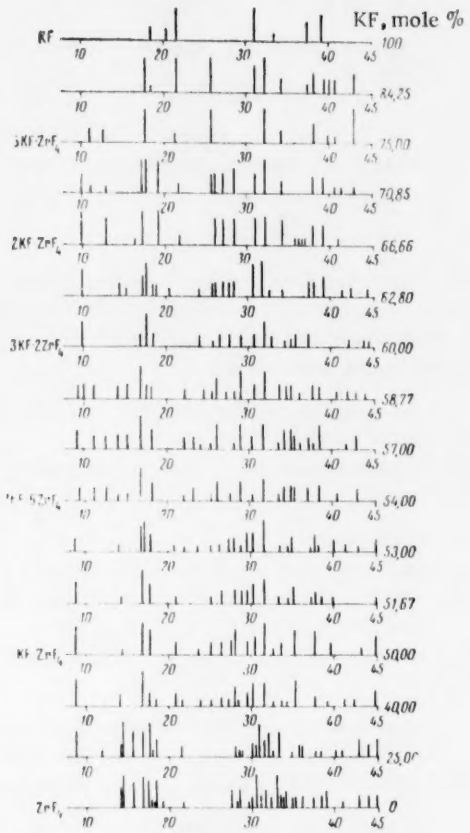

Fig. 2. Line diagrams of the compounds in the system $KF-ZrF_4$.

The zirconium fluoride synthesized by us was the monoclinic modification, described in [5]. Endothermic effects at 612 and 685° were found on its heating curve, corresponding to the transformations in the solid state. On reheating, the effect at 612° disappeared.

Due to the great volatility of ZrF_4 when heated, a marked deflection of the differential curve is observed on the thermogram beginning with 880°. The endothermic effect, corresponding to the melting of ZrF_4, is found at 903 ± 5°. If the covered platinum crucible with ZrF_4 is introduced into the furnace, previously heated to 930-940°, and after this, having turned off the furnace, the cooling curve is recorded, then the effect of the solidification of ZrF_4 is observed at 903 ± 5°; with further cooling a polymorphous transformation takes place at 685°. According to our data, potassium fluoride melts at 850°. The following compounds K_3ZrF_7, $K_5Zr_2F_{13}$, K_2ZrF_6, $K_3Zr_2F_{11}$, $K_7Zr_6F_{31}$, and $KZrF_5$ were detected in the system $KF-ZrF_4$. The fluorozirconates K_3ZrF_7 and $KZrF_5$ melt congruently at 923 and 455°, respectively. The fluorozirconates $K_5Zr_2F_{13}$ and K_2ZrF_6 are formed by the peritectic reactions:

$$K_3ZrF_7 + \text{molten } (KF, ZrF_4) \rightleftarrows K_3Zr_2F_{11}.$$

$$K_3ZrF_7 + \text{molten } (KF, ZrF_4) \rightleftarrows K_2ZrF_6.$$

The fluorozirconates $K_3Zr_2F_{11}$ and $K_7Zr_6F_{31}$ exist only in the solid state below 327 and 380°, respectively. The eutectic between KF and K_3ZrF_7 lies at 760° and 13% ZrF_4, that between K_3ZrF_7 and $KZrF_5$ lies at 430° and 47% ZrF_4, and that between $KZrF_5$ and ZrF_4 lies at 440° and 60% ZrF_4.

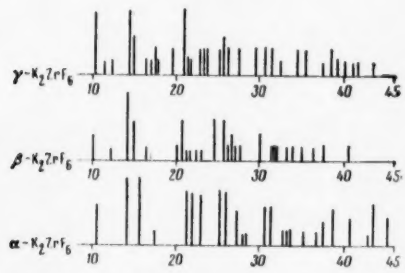

Fig. 3. Line diagrams of the α-, β-, and γ-modifications of K_2ZrF_6.

Several modifications were detected for the fluorozirconate K_2ZrF_6 (Fig. 3). The transformations of K_2ZrF_6 can be depicted by the scheme:

$$\alpha\text{-}K_2ZrF_6 \overset{240^\circ}{\rightleftarrows} \delta\text{-}K_2ZrF_6 \overset{218^\circ}{\rightleftarrows} \gamma\text{-}K_2ZrF_6 \overset{445^\circ}{\rightleftarrows}$$

$$\rightleftarrows \delta\text{-}K_2ZrF_6 \overset{585^\circ}{\rightleftarrows} \text{liq.} + K_3ZrF_7.$$

The fluorozirconate $KZrF_5$ undergoes polymorphous transformations at 400 and 424°. The fluorozirconate of composition $K_3Zr_2F_{11}$ undergoes polymorphous transformation at 313°. K_3ZrF_7 has one modification, which crystallizes in the face-centered cubic lattice a = 8.966 ± ± 0.003kX, and forms a solid solution with K_2ZrF_6 (in the region of 73-75% KF).

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IRON-HAFNIUM COMPOSITION DIAGRAM

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Hafnium is a difficultly fusible rare metal. Its properties have not been studied very well as yet, because until recently it has not been possible to obtain it without a considerable quantity of contaminants (mainly zirconium). The melting point of hafnium has not been identified; thus, according to the literature data it is: 2230° [1], 1975 ± ± 25° [2], 2222± 30° [3], 2130 ± 15° [4]. An allotropic transformation occurs in hafnium, the temperature of which also has not been established accurately up to the present time. Thus, according to the data of several investigations the temperature of the allotropic transformation in hafnium is: 1310 ± 10° [5], 1500° [6], 1750 ± 20° [7], 1950 ± 100° [8]. Like zirconium, the low-temperature form of hafnium has a closely packed hexagonal lattice, and the high-temperature form has a cubic volume-centered lattice.

We have not found any information in the literature sources on the composition diagram of the system iron–hafnium. There is only contradictory information on the intermetallide Fe_2Hf. In an article [9] it is indicated that the intermetallide has two polymorphic modifications. The high-temperature form has a hexagonal lattice (a = 4.952, c = 8.087 kX) and is observed in samples chilled from a temperature of 1600°. The low-temperature form has a cubic lattice (a = 7.011 kX) and is observed in samples chilled from temperatures of 600-1400°, along with a small amount of the high-temperature form.

In [10] by the same author, the existence of a low-temperature modification in the intermetallide Fe_2Hf is not confirmed, and it is indicated only that the crystal lattice of the intermetallide is hexagonal of the $MgZn_2$ type, and has the parameters a = 4.970, c = 8.109 kX. The melting point of the intermetallicle is 1650°.

In a report that appeared recently [11] it is indicated that the solubility of hafnium in α-iron is approximately 0.2% by weight.

Preparation of Alloys and Methods of Investigation

Most of the alloys were prepared from electrolytic iron purified by tempering in hydrogen and then in vacuum. Fusion of this iron into compact samples was carried out in an arc furnace. Part of the alloys were prepared from iron carbonyl. After the indicated purification of the iron, its carbon, silicon, manganese, sulfur, phosphorus, and nitrogen content did not exceed 0.01% of each.

For the second component of the alloys, metallic hafnium iodide was used, the main impurities in which were 0.5% zirconium and 0.2% molybdenum. The alloys were prepared in an arc furnace [12] in an atmosphere of pure argon. To attain homogeneity of the ingot, fusion was repeated 5-6 times. Twenty-five alloys were prepared in all. The hafnium and carbon content of the alloys was checked by chemical analysis, the results of which are given in the table.

Thermal analysis of the alloys was carried out in an apparatus described in [12], using a tungsten–iridium thermocouple and WR 5/20 (W + 5% Re–W + 20% Re). Dilatometric analysis was carried out with the apparatus described in [12]. For work up to 1000-1100° a chromel–alumel thermocouple was used, and for 1100-1500° a platinum platinorhodium couple was used. The conversion temperatures in the alloys obtained by the indicated methods may differ from the equilibrium values, since they were determined under conditions of continuous heating at a rate of 20-30° per min in thermal analysis and 0.2-3°/min in dilatometric analysis. We considered as close enough to the equilibrium values those values of the conversion temperatures which were obtained under conditions of very slow heating.

Interpretation of the phase components of the alloys was accomplished with the aid of x-ray analysis. The radiograms were made with filtered cobalt K α-irradiation in a cylindrical camera with a diameter of 143.4 mm.

Magnetic analysis (determination of the Curie point) of the alloys was carried out in an Akulov anisometer by the differential method described in [13].

Expt. No.	Hf wt-%	C wt-%	Expt. No.	Hf wt-%	C wt-%	Expt. No.	Hf wt-%	C wt-%
1	0,01		9	1,08	0,010	17	28,70	0,010
2	0,02	0,008	10	1,85	0,007	18	45,27	
3	0,044	0,008	11	3,34	0,011	19	60,90	
4	0,048	0,008	12	5,67	0,007	20	70,40	
5	0,15	0,008	13	8,75	0,010	21	81,25	
6	0,16	0,007	14	14,99	0,008	22	90,85	
7	0,26	0,009	15	20,85	0,010	23	94,0	
8	0,53	0,007	16	25,15	0,007	24	97,0	

DISCUSSION OF RESULTS

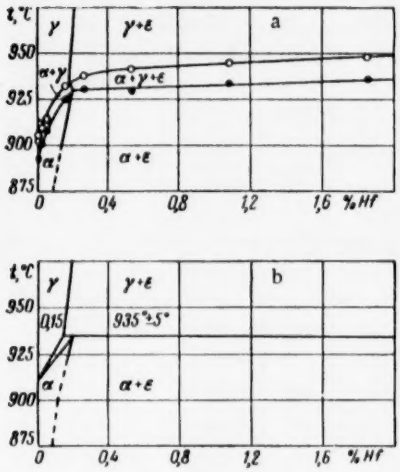

Fig. 1.

By the methods of differential thermal and dilatometric analysis it was established that in alloys containing up to 45% hafnium there are 4 transformations in the solid state. Two of these are magnetic—in α-iron, and in the intermetallide, the third is associated with the conversion of α-iron to γ-iron, and the fourth with the conversion of γ-iron to δ-iron. The temperature of the conversion $\alpha \rightarrow \gamma$ was determined by the dilatometric method with heating at a rate up to 0.5° per min. In Fig. 1a the experimental data are presented. The solid points represent the temperature of the beginning of the transformation and the circles represent the final temperature of the transformation. On the basis of these data we worked out the portion of the iron—hafnium diagram shown in Fig. 1b.

The $\alpha \rightarrow \gamma$ conversion in the starting iron, which contained up to 0.01% of carbon, was observed on heating at a rate of 0.2-0.3°/min in the temperature range 894-905°. From the thermograms and dilatograms for heating and cooling of the alloys, it was not possible to distinguish the conversions $\alpha + \epsilon \rightarrow \gamma + \epsilon$ from $\alpha \rightarrow \gamma$. The maximum solubility of hafnium in α-iron (the peritectoid point) is 0.2%, determined by the intersection of the peritectoid contour line with the extrapolated curve of the $\alpha \rightarrow \gamma$ conversion. A characteristic property is the increase in the temperature of the conversion $\alpha + \epsilon \rightarrow \gamma + \epsilon$ with an increase in the hafnium content of the alloys and the extension of the conversion over an appreciable temperature range.

The conversion temperature for $\alpha + \epsilon \rightarrow \gamma + \epsilon$, which is 935 ± 5°, therefore was determined from the dilatogram of the two-phase alloy ($\alpha + \epsilon$) closest in composition to the peritectoid point.

The conversion $\gamma + \epsilon \rightarrow \delta$ is accomplished by a eutectoid reaction at 1330 ± 5°. The composition of the eutectoid alloy is 2.8% hafnium. The maximum solubility of hafnium in γ-iron is 1.6% at 1330°. In alloys containing from 70 to 99% of hafnium, two conversions were discovered in the solid state. The first is associated with the magnetic conversion of the intermetallide and is accompanied by an essential change in the coefficient of thermal expansion. The second conversion in the above-mentioned alloys is euctectoid and occurs at 1235 ± 10° according to the reaction $\epsilon + \alpha_{Hf} \rightleftharpoons \beta_{Hf} + \epsilon$.

It is accompanied by an appreciable heat effect and a considerable increase in volume (on heating). This eutectoid transformation also is observed in the alloy containing 99% hafnium. Consequently the solubility of iron in hafnium is small and known to be less than 1%. The fusion diagram was constructed exclusively by the method of differential thermal analysis. In this way it was established that in the system iron—hafnium there are two eutectic transformations: $L \rightleftharpoons \delta + \epsilon$ at 1350 ± 10° and $L \rightleftharpoons \beta_{Hf} + \epsilon$ at 1300 ± 10°. The hafnium content in the eutectic alloys is 21.5 and 85%, respectively.

X-ray structural analysis of alloys No. 17 to 22, into the phase composition of which the intermetallide Fe_2Hf (ε-phase) enters, showed that the crystal lattice of the ε-phase is hexagonal, of the $MgZn_2$ type. The parameters

of the crystal lattice of the ε -phase were determined from the lines (226), (233), (118), and (232). These parameters proved to be different for alloys of different composition, specifically:

Parameters	a	c	c/a
Alloy No. 18	4.9116	8.0013	1.629
Alloy No. 19	4.9565	8.0964	1.6335
Alloy No. 21	4.9756	8.1288	1.6338

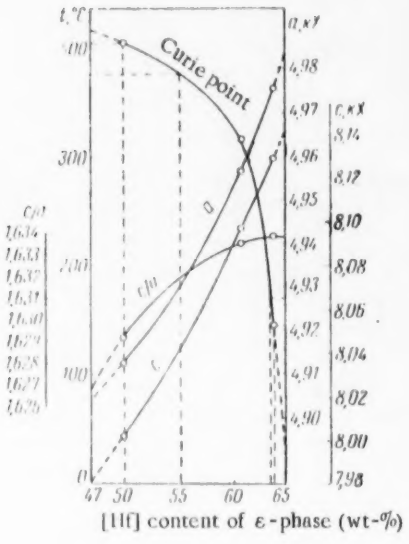

Fig. 2.

The parameters of the crystal lattice of the ε -phase of alloy No. 17 practically coincide with the parameters of the ε -phase of alloy No. 18. Coincidence of the parameters of the ε -phase was established also for alloys No. 20-22. Preliminary treatment of these alloys consisted in annealing at 1200° with subsequent chilling. Inasmuch as alloys No. 17 and 18 are two-phase (α + ε), when they were annealed the maximum iron concentration at the given temperature was established in the ε -phase. In alloys No. 20-22 the phase α_{Hf} was present besides the ε -phase, and therefore on annealing the maximum possible solubility of hafnium at the given temperature was established in these alloys.

The difference in the parameters of the crystal lattice of the ε -phase in the several alloys indicates the existence of an appreciable region of homogeneity of the ε -phase. Determination of the limits of the single-phase region of the intermetallide at 1200° was carried out by the direct determination of the hafnium content in the ε -phase in alloys No. 17, 18, and 21, annealed at 1200°. The chemical composition of the ε -phase was determined by I. D. Marchukova by the method of local x-ray spectral analysis in an RSASh-2 apparatus at the Institute of Metallurgy of the Academy of Sciences of the USSR.

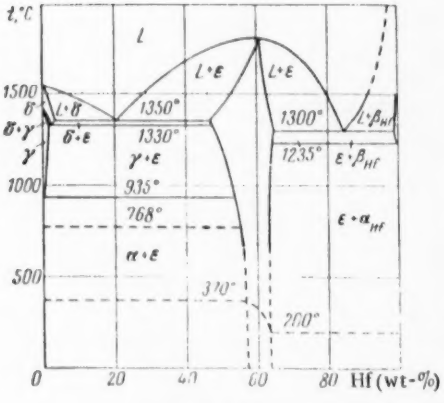

Fig. 3.

The hafnium content in the ε -phase of alloy No. 18 was determined to be 50%, and in the ε -phase of alloy No. 21 it was 64%. In Fig. 2 the relationship of the parameters a, c, and c/a of the lattice of the ε -phase to the composition of the intermetallide is shown. As indicated above, it was established that the intermetallide F_3Hf is ferromagnetic. The Curie point was determined for the ε -phase in different alloys, i.e., for a different ε -phase composition, by magnetic analysis. Thus it was established that with a change in the hafnium content of the intermetallide from 50 to 64% the Curie point is lowered from 405 to 145° (Fig. 2). As a result of prolonged (above 100 hr) annealing of the alloys at 850° the composition of the ε -phase was changed in them, and the Curie point also was changed. In alloy No. 18 the Curie point was lowered (in comparison with the condition after annealing at 1200°) from 405 to 377°, and in alloy No. 21 it was raised from 145 to 170°. This change in the Curie point occured as a result of an increase in the hafnium content in the ε -phase of alloy No. 18 from 50 to 55% and a decrease in the hafnium content of the ε -phase of alloy No. 21 from 64 to 63.5% (see Fig. 2). By this means the limits of the single-phase region of the intermetallide were designated.

The hardness of the intermetallide, which was determined with a Vickers apparatus, was 650 kg/mm², and its melting point was 1810 ± 20° (for a composition corresponding to the stoichiometric composition of Fe_2Hf). This temperature is considerably higher than that obtained in [10] (1650°).

The composition diagram of the system iron–hafnium constructed from the results of the present work is given in Fig. 3.

In conclusion, we consider it our pleasant duty to express our appreciation to I. B. Borovskii for carrying out the local x-ray spectral analysis in his laboratory and for the direction given in this.

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POLYMERIZATION OF STYRENE, BUTADIENE, AND ISOPRENE INITIATED BY ETHYLLITHIUM IN VARIOUS MEDIA

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In this work we investigated the separate and the joint polymerization of styrene, butadiene, and isoprene initiated by ethyllithium in toluene, triethylamine, diethyl ether, dioxan, and tetrahydrofuran (THF) in order to determine the relationship of the reactivity of these monomers to their structure and the conditions of polymerization. The experimental methods were described in preceding articles [1, 2].

In the polymerization of styrene, butadiene, and isoprene the molecular weight of the polymers increased with the extent of polymerization in all of the solvents studied, and the relationship of the molecular weight to the concentration of the components was close to mole wt. = M/C [3, 4]. When investigations were carried out in the range of low concentrations of the initiator, $\sim 10^{-5}$ mole/liter, the walls of the dilatometer were specially treated. Under these conditions the concentration of the active centers was determined from data on the molecular weight. In the presence of electron-donor solvents the polymerization was carried out in one-piece quartz cell-dilatometers and the concentration of active centers was determined spectrophotometrically at a selected wavelength.

1. Polymerization in toluene. In carrying out the polymerization of styrene, isoprene, and butadiene in toluene even at comparatively low concentrations of the initiator, deviation from a proportional relationship between the rate and the concentration of the initiator was observed. The rules followed have been explained previously [1] by the formation in hydrocarbon media of reciprocally associated "live" polymers, which are inactive in polymerization. Other authors also have come to a similar conclusion in investigating the kinetics of polymerization of styrene [4, 5] and isoprene [6]. The presence of the association of active centers also has been confirmed by viscosimetry. It was found that the viscosity of solutions of "live" Li-polyisoprene in toluene is considerably lowered by deactivation of the active centers.

With an increase in temperature the equilibrium between the associates and the monomeric centers which are active in polymerization is shifted in the direction of the latter, which is due to the lowering of the energy of activation of the process. Even at concentrations of the initiator of $\sim 0.5 \cdot 10^{-4}$ mole/liter the energy of activation of the polymerization process for styrene is decreased with an increase in temperature (Table 1, Nos. 1, 2), which indicates the presence of association under these conditions. The values obtained previously for the energy of activation of the polymerization of styrene with initiator concentrations of ~ 0.01 mole/liter [1] corresponds to systems with a considerable portion of associated active centers.

As can be seen from the data of Table 1, the change in rate of polymerization with a decrease in concentration of the initiator is shown to the greatest extent in the polymerization of styrene (Expt. Nos. 1, 3) and to the least extent in the polymerization of butadiene (Nos. 13 and 14). This indicates that the association of the active centers increases in the order: lithium-polystyrene < lithium-polyisoprene < lithium-polybutadiene.

On the basis of the data on the composition of the copolymers and the constants of copolymerization of the system butadiene–styrene in toluene (see Table 2) and the previously obtained data for the system isoprene–styrene [1], the relative reactivity of the monomers increases in the order styrene < isoprene < butadiene.

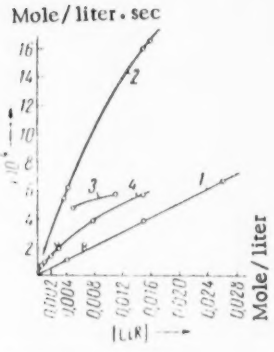
2. Polymerization in the presence of electron-donor solvents. When ether, dioxan, triethylamine, or THF was introduced as an additive to the hydrocarbon solvent, the rate of polymerization of styrene, isoprene, and butadiene increased and the energies of activation of the processes correspondingly decreased (Table 1).

TABLE 1

Expt. No.	Medium	Additive	Additive, vol-%	[LiR], mole/liter	Temperature range of polymerization, °C	V_1, mole/liter · sec at + 30°	E^2 Cal mole	Log A liters/moles · sec	K, liters moles · sec
Polymerization of styrene									
1	Toluene	—	—	$0{,}5\cdot10^{-4}$	+33, +47,5	$0{,}40\cdot10^{-4}$	14,0	—	
2			—	$0{,}5\cdot10^{-4}$	+60, +72	$0{,}57\cdot10^{-4}$	11,6	—	
3[3]			—	$3\cdot10^{-3}$	+ 7, +22	$0{,}7\cdot10^{-3}$	14,6	—	
4[3]			—	$4\cdot10^{-2}$		$0{,}4\cdot10^{-2}$		—	
5		Ether	38	$0{,}7\cdot10^{-2}$	−15, + 5	—	13,3		
6			30	$1{,}15\cdot10^{-2}$	− 2, +15	—	13,4	9,0	$2{,}5\cdot10^{-4}$
			30	$0{,}3\cdot10^{-2}$	− 2, +15	—	13,1	8,7	$2{,}5\cdot10^{-4}$
7		Dioxan	27	$0{,}8\cdot10^{-2}$	−17, − 4	—	13,0	8,8	$3{,}7\cdot10^{-4}$
8		Amine	30	10^{-4}÷$3\cdot10^{-2}$	−40, 0	—	11,2	8,65	$1{,}26\cdot10^{-2}$
9		THF	0,6	$5\cdot10^{-3}$	−25, −10	—	6,8	4,46	$1{,}15\cdot10^{-2}$
10			2,3	$4\cdot10^{-3}$	−55, −30	—	5,8	3,95	$3{,}1\cdot10^{-2}$
11			8	$5\cdot10^{-3}$	−60, −40	—	4,5	3,6	$24\cdot10^{-2}$
12			15	$5{,}4\cdot10^{-3}$	−70, −55	—	4,1	3,5	$44\cdot10^{-2}$
Polymerization of butadiene									
13[3]	Toluene	—	—	0,005—0,02	+20, +45	$1{,}2\cdot10^{-4}$	20,5	—	—
14		—	—	10^{-5}	+35, +55	$0{,}4\cdot10^{-4}$	16,9	—	—
15	Hexane	Amine	35	0,004	− 3, +20	$4{,}8\cdot10^{-4}$	13,9	—	—
16			35	0,011	− 3, +20	$5{,}7\cdot10^{-4}$	14,4	—	—
17			80	~0,0001	+15, +35	—	12,1	—	—
18		THF	28	0,003	−38, −20	$0{,}19\cdot10^{-4}$*	10,7	—	—
19			80	0,0045	−60, −25	$0{,}25\cdot10^{-3}$*	7,3	—	—
			80	0,001	−40, −25	$0{,}7\cdot10^{-4}$*	6,3	—	—
Polymerization of isoprene									
20	Toluene	—	—	$2{,}3\cdot10^{-5}$	+27, +40	$0{,}54\cdot10^{-4}$	14,7	—	—
21		—	—	$6{,}0\cdot10^{-5}$	+27, +47	$1{,}0\cdot10^{-4}$	15,3		
22		—	—	$1{,}2\cdot10^{-4}$	+27, +40	$1{,}2\cdot10^{-4}$	16,8		
23		—	—	$5{,}0\cdot10^{-4}$	+27, +40	$1{,}6\cdot10^{-4}$	17,9		
24[3]		—	—	$1{,}3\cdot10^{-3}$	+27, +44	$1{,}9\cdot10^{-4}$	18,8		
25[3]		—	—	>0,005	—	$2{,}1\cdot10^{-4}$	19,5		
26	Amine	—	—	0,0038	+11, +30	$5{,}5\cdot10^{-4}$	10,9		
27		—	—	0,0043	+10, +40	$6{,}2\cdot10^{-4}$	10,6		
28		—	—	0,015	+11, +30	$16\cdot10^{-4}$	10,9		
29		—	—	0,016	+10, +40	$16{,}5\cdot10^{-4}$	—		
30[4]	THF	—	—	—	−60, −45	—	5,5		
31[4]		—	—	—	−45, −20	—	7,0		
32[4]		—	—	—	−21, −10	—	8,7		
33[4]		—	—	—	−10, +14	—	9,8		
34[4]		—	—	—	+14, +27	—	13,0		

[1]The rates referred to unit concentration of the monomer (V) and the rate constants of polymerization (K) were calculated from the values of the rates obtained in the temperature range indicated in the table. [2]The values given for the energy of activation are averaged values of the data on the energy of activation determined in the course of the process by means of the change in temperature of the polymerization at different degrees of conversion. The rates of polymerization in all cases were proportional to the concentration of the monomer, except for the polymerization of isoprene in THF, where a small deviation was observed from the proportional relationship. [3]The experiments on polymerization initiated by the "live" polymer Li-polystyrene gave similar values for the energies of activation (the decrease in E did not exceed 1 cal) and the rates. [4]The values of E in Experiments Nos. 30-34 were obtained by means of the successive change in temperature in the course of the same process. * At −40°.

The most distinct effect was observed in the presence of THF, which has the greatest electron-donor properties. In the presence of a very small addition of THF, 0.6%, the energy of activation of polymerization of styrene in toluene was decreased from 14.5 to 6.8 cal/mole. The energy of activation for butadiene on going from toluene to a mixture of toluene with 30% THF also sharply decreased (Table 1, Nos. 13, 18). When isoprene was polymerized in THF there was an increase in the energy of activation, which was determined in the course of the process, with the increase in temperature (Table 1, Nos. 30-34), which is explained apparently by the presence of degenerated chain transmittal through the monomer [6].



Rate of polymerization vs. concentration of initiator. In amine: 1) styrene at −34°; 2) isoprene at +30°; 3) butadiene at +30° and in THF; 4) butadiene at −39°.

In the presence of electron-donor solvents, as a result of the formation of complexes of them with lithium, the association of "live" polymers is decreased. As follows from Table 1 and the figure, association of lithium-polystyrene does not occur in electron-donor solvents (a proportional relationship is observed between the rate of polymerization and the concentration of initiator), lithium-polyisoprene is associated to a small extent in the amine, and lithium-polybutadiene shows a considerable degree of association in the amine. Even in THF, a solvent with a high solvating capacity, some association of lithium-polybutadiene is observed. These data confirm the relationship obtained in the hydrocarbon medium for the degree of association of the active centers to their structure.

In previous work the characteristics of the mechanism of polymerization of nonpolar monomers initiated by ethyl lithium in hydrocarbon media was explained by the participation of the lithium components, along with the carbonium ion in the act of chain growth [7, 1].

Introduction of electron-donor additives, which form complexes with the lithium component of the catalyst, leads to a decrease in the effect of this component on the act of chain growth. In accordance with this, the mechanism of the process is changed, approaching, in the presence of additives with high solvating capacity (THF), the processes of typical anion polymerization. With an increase in the concentration of THF an increase is noted in the rate of polymerization of styrene and butadiene and a corresponding decrease in the energy of activation of the process. It might be thought that the decrease in energy of activation with an increase in THF concentration occurs both as a consequence of the destruction of the associates formed by the active centers and as a result of a change in the structure of the complexes of THF with the active centers and as a result of a change in the structure of the complexes of THF with the active centers and an increase in the dielectric constant of the medium. The effect of the dielectric constant of the medium, however, hardly has a determining effect, since very small additions of THF cause a sharp decrease in the energy of activation in the polymerization of styrene.

TABLE 2. Copolymerization

Expt. No.	System	Medium	Temp. °C	Constants of copolymerization		Amt. of styrene (mole-%) in copolymer with 1 : 1 ratio
				r_1	r_2	
1	Styrene (1) – butadiene (2)	Toluene	25	0,1	12,5	9,0
2		Amine 40%	25	0,3	5,5	20
3		Ether 40%	25	—	—	33
4		THF	−35	8±1	0,2±0,1	85
5	Styrene (1) – isoprene (2)	Toluene	27	0,25	9,5	12
6		Amine	27	0,8	1,0	48
7		THF	27	9	0,1	82
8		"	−35	40	0	97

It is interesting to note that polymerization of styrene in ether and dioxan, in spite of the different dielectric constants of these solvents (4.33 and 2.28 at 20°), proceeds with similar rates and energies of activation.

The compositions of the copolymers of the systems styrene–isoprene and styrene–butadiene were investigated in the presence of electron-donor solvents. For the amine solvent and THF the constants of copolymerization were calculated from data on the composition of the copolymers (Table 2).

On copolymerization of the systems isoprene-styrene and butadiene-styrene when electron-donor solvents are introduced the relative proportion of styrene in the copolymer increases. From the data obtained it can be seen that the effect of the solvents on separate and joint polymerization is not always similar (see, for example, the polymerization of styrene in the presence of the amine and ether). In the presence of THF the compositions of the copolymers are greatly enriched in styrene and correspond to the compositions obtained in typical anionic processes [8].

According to the data of Table 2, the relative reactivity of the monomers in THF increases in the order: isoprene < butadiene < styrene.

The relatively small deviation from the proportional relationship of the rate of polymerization of isoprene in the amine and of butadiene in THF to the concentration of the initiator permits the assumption that the reactivity of the monomers in separate polymerization in polar media changes in the same order as in joint polymerization.

The effect of the solvents studied on the polymerization processes depends essentially on their electron-donor capacity. Relatively weak electron-donor solvents – the amine, ether, and dioxan – on reaction with lithium apparently make little change in the polarization of the Li–C bond. In individual cases they even increase the energy of activation of chain growth in comparison with hydrocarbon solvents, as occurs in the polymerization of styrene (Table 1, Nos. 2, 5, 7). However, solvents of high electron-donor capacity (THF), completely cutting out the effect of the lithium, sharply increase the polarization of the Li–C bond, which correspondingly makes the process approximate the rules for a typical anionic polymerization in which the carbonium ion is the active center.

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PREPARATION AND SOME PROPERTIES OF METALLIC SCANDIUM

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Metallic scandium has already been prepared in small amounts by many investigators [1-9], but its properties have been little studied up to the present time. The present work is devoted to the preparation of metallic scandium from its anhydrous chloride [10] and the study of some of its properties.

The starting compound in this work was spectrally pure scandium oxide prepared from the technical oxide by methods of thiocyanate extraction and precipitation of scandium oxalate [11]. Anhydrous scandium chloride was prepared by chlorination of a mixture of scandium oxide and sugar charcoal in 3:1 weight ratio. The chlorination process was carried out in a quartz tube at 1000°; the scandium chloride formed was sublimed and condensed on the colder parts of the apparatus. The freshly prepared $ScCl_3$ was reduced with metallic calcium at 900° in an atmosphere of pure argon. The reaction mixture containing a small excess of calcium (~5 wt-%) was placed in a tantalum crucible. The reaction products obtained, which usually contained Ca, CaO, $ScCl_3$, and also Si as contaminants, were ground to a powder with a particle size of < 0.2 mm and were treated subsequently with water to dissolve the $CaCl_2$, Ca, CaO, and $ScCl_3$, with 10% sodium hydroxide solution to remove silicon, again with water, and finally with methyl alcohol and ether. In all cases the separation of the solvents was carried out by decantation. The powdered metallic scandium obtained was dried in the air (10-15 min) and then in vacuum (10^{-4} mm Hg) until the volatile contaminants were completely removed (~30 min).

Fusion of the metallic scandium was carried out under reduced pressure of argon (200 mm Hg) in an arc furnace with a water-cooled copper bottom plate and a movable tungsten electrode [7, 8]. The metal was first pressed into tablets under a pressure of 100 kg/cm^2 and was heated at 500-600° in a high vacuum ($10^{-5} - 10^{-6}$ mm Hg).

The fused metallic scandium was a lustrous metal of a silver color with a characteristic yellow shade.

According to an analysis carried out by the hydrogen method, the product contained 97-97.5 wt-% of metallic scandium. The total scandium content, which was determined by gravimetric and volumetric methods, was 98-99 wt-%. In the gravimetric determination the sample was brought into solution, from which scandium hydroxide then was precipitated; the formula by weight was Sc_2O_3. The volumetric determination was carried out by titration of the trivalent scandium with Trilon B with reference to murexide [12]. The gravimetric and volumetric analyses gave results in good agreement. In most samples of the metal the presence of small amounts of silicon (0.1 wt-%) and calcium (< 0.001 wt-%) were detected spectrally. In the case where scandium oxide of > 99% purity was used as the starting material, the metal obtained contained traces of Zr, Th, Y, Yb and Fe (total < 0.1 wt-%). Chlorine was determined by nephelometric reaction with $AgNO_3$. In some samples the oxygen content was determined. The results of analysis* of the fused metallic scandium were as follows (in percent): metallic scandium 97-97.5; total scandium content calculated as the element 98-99%; chlorine < 0.05; calcium < 0.001; silicon 0.1; oxygen < 0.9; total Zr, Th, Y, Yb, Fe < 0.1.

For further purification the fused metallic scandium was sublimed in high vacuum ($10^{-5} - 10^{-6}$ mm Hg) from a tantalum crucible onto a tantulum plate at 1500-1600°. Heating was accomplished with the aid of a high-frequency apparatus with a tube generator. The metallic scandium content of the sublimate was > 99%. For the samples of metallic scandium obtained a study was made of the crystalline structure, some mechanical properties, the stabiltiy in air, and also the kinetics of solution in hydrochloric acid.

The study of the structure of metallic scandium is of interest in view of the fact that the existence of its cubic modification (a = 4.5 kX) [6, 13] has not been finally established. X-ray investigation was carried out on a sample

* The average values of the analyses of different lots of the metal are given here.

of the metal sublimed in vacuum. The x-ray photographs were taken with an electron tube with a copper anode. The results of the x-ray analysis are given in Table 1.* All 29 lines of the photograph are well indicated in a hexagonal lattice of the magnesium type with a = 3.302 ± 0.005 kX and c = 5.255 ± 0.005 kX, c/a = 1.591, Z = 2. The x-ray density was 2.992 g/cm^3; the value 3.0 g/cm^3 was found by the picnometer method. Comparing the results obtained with the literature data [8, 9], we can conclude that scandium crystallizes only in a hexagonal lattice. The cubic phase observed by Meisel [13] and Achard [6] probably was due to considerable contamination of the metal, most likely by scandium nitride ScN, which crystallizes in cubic syngony with a = 4.44 kX [14].

TABLE 1. Results of X-Ray Investigation on Metallic Scandium

Expt. No.	Intensity	hkl	$1/d^2$, kX^{-2} Found	$1/d^2$, kX^{-2} Calc.*	$\left(\frac{1}{d^2_{found}} - \frac{1}{d^2_{calc.}}\right)$ kX^{-2}	Expt. No.	Intensity	hkl	$1/d^2$, kX^{-2} Found	$1/d^2$, kX^{-2} Calc.*	$\left(\frac{1}{d^2_{found}} - \frac{1}{d^2_{calc.}}\right)$ kX^{-2}
1	4	100	0,1234	0,1223	+0,0011	16	2	114	0,9449	0,9462	−0,0013
2	2	002	0,1458	0,1448	+0,0010	17	2	212	1,001	1,001	0
3	5	101	0,1602	0,1585	+0,0017	18	1	105	1,027	1,027	0
4	4	102	0,2677	0,2671	+0,0006	19	1	204	1,070	1,068	+0,002
5	4	110	0,3690	0,3669	+0,0021	20	3	300	1,101	1,101	0
6	4	103	0,4488	0,4481	+0,0007	21	4	213	1,182	1,182	0
7	2	200	0,4898	0,4892	+0,0006	22	4	302	1,245	1,245	0
8	4	112	0,5129	0,5117	+0,0012	23	1	006	1,301	1,303	−0,002
9	4	201	0,5267	0,5254	+0,0013	24	2	205	1,393	1,394	−0,001
10	2	004	0,5810	0,5793	+0,0017	25	3	214	1,434	1,435	−0,001
11	2	202	0,6333	0,6340	−0,0007	26	3	220	1,467	1,467	0
12	2	104	0,7018	0,7016	+0,0002	27	2	310	1,590	1,590	0
13	3	203	0,8158	0,8150	+0,0008	28	3	222	1,611	1,612	−0,001
14	1	210	0,8555	0,8560	−0,0005	29	5	311	1,625	1,626	−0,001
15	5	211	0,8940	0,8922	+0,0018						

*a = 3.302 kX, c = 5.255 kX.

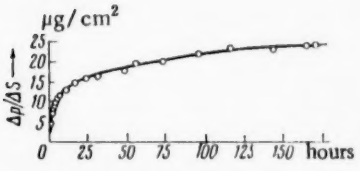

Fig. 1. Kinetics of oxidation of metallic scandium in air at 20°.

For a rating of the mechanical properties of metallic scandium, the microhardness and the yield strength were studied. The microhardness was measured on an apparatus with a diamond pyramid. The microhardness of 97-97.5% metallic scandium was 145 ± 10 kg/mm^2, for a sample of > 99% purity this value fell to 75 ± 5 kg/mm^2, i.e., almost by half. The value of the microhardness obtained by us for metallic scandium of > 99% purity agrees well with the literature data [15].

For the determination of the yield strength, samples of a definite shape with the diameter of the working part 2 mm were turned from the fused metallic scandium. It should be noted that metallic scandium machines well. Measurements of the yield strength were carried out on a breaking machine at an average rate of introduction of the load of 3 kg/sec·mm^2. The yield strength of 97-97.5% scandium was 25-30 kg/mm^2. With a higher content of nonmetallic contaminants the yield strength of the metal was greatly lowered.

The stability of 97-97.5% metallic scandium in air was studied by two methods: isothermically at 20° and polythermically in the temperature range 20-800°. In the first case the oxidation of the metal was studied by a kinetic method on a dampered quartz balance with a sensitivity of 1 μg/division [16].** The results of one of the experiments are given in Fig. 1, from which it is seen that in 170 hr the surface of the metal was covered with a film of oxide ~600 A thick, and the process of oxidation of the metal had practically ceased.

* The authors express their appreciation to Yu. P. Simanov for his valuable advice in the consideration of the results of the x-ray analysis of metallic scandium.

** The measurements were made in the Institute of Physical Chemistry of the Academy of Sciences of the USSR with participation of V. A. Arslambekov.

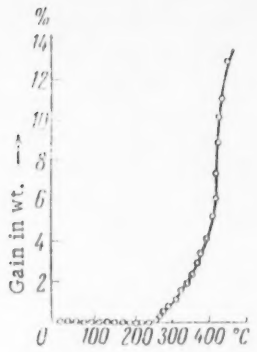

Fig. 2. Oxidation of metallic scandium on heating in air (average rate of heating 3°/min).

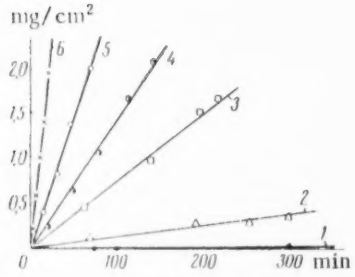

Fig. 4. Kinetics of reaction of metallic scandium with aqueous solutions of HCl of different concentrations; 1) 0.001 N, $K < 5 \cdot 10^{-5}$ mg/cm² · min; 2) 0.005 N, K = 0.001; 3) 0.01 N, K; 0.007; 4) 0.02 N, K = 0.015; 5) 0.05 N, K = 0.03; 6) 0.1 N, K = 0.1.

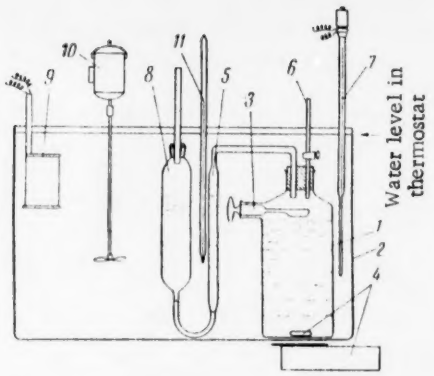

Fig. 3. Diagram of apparatus for study of reaction of metallic scandium with aqueous solutions of HCl: 1) reaction flask; 2) glass thermostat; 3) "spoon" with ground joint; 4) magnetic stirrer; 5) buret; 6) stopcock for connection of flask with the atmosphere; 7) contact thermometer; 8) funnel for bringing apparatus to atmospheric pressure; 9) heater; 10) stirrer; 11) thermometer.

The oxidation of 97-97.5% scandium by heating in the air was studied on a continuously weighing balance. The powdered metal (< 0.2 mm) was placed in a small quartz cup which was hung on the balance by a platinum wire. The weight of the sample was measured, in the process of heating, with an accuracy of ± 0.5 mg. A typical curve for the change in weight of the metal versus the temperature is shown in Fig. 2 (average rate of heating 3°/min). Appreciable oxidation of the metallic scandium in air started at 250°. Beginning with this temperature the curve for the change in weight rises sharply upward. In the range 20-200° the metal is practically unoxidized. Thus, keeping the powdered metallic scandium in the air at 200° for 20 hr did not result in a change in weight.

The kinetics of the reaction of metallic scandium with aqueous solutions of HCl were studied at 25 ± 0.1° in an apparatus for which the diagram is shown in Fig. 3.* Plates of the fused metal with an apparent surface of 3-4 cm² and a weight of 0.3-0.5 g served as samples. The rate of solution of the metal was recorded by the amount of hydrogen evolved and the total amount of scandium dissolved during the entire experimental period verified also by the loss in weight of the sample. The two determinations gave concordant results. The data obtained in several experiments are shown in Fig. 4.

For each concentration of HCl the rate constant of solution K (mg/cm² · min) was calculated graphically. The reaction of metallic scandium with aqueous solutions of HCl proceeded rather rapidly at a concentration of the latter of 0.05-0.1 N and higher. With a decrease in concentration of the HCl the rate of solution of the metal fell sharply and in 0.001 N HCl the constant of solution of the metal was extremely small ($< 5 \cdot 10^{-5}$ mg/cm² . min). It therefore must be considered that there is practically no solution of metallic scandium in 0.001 N HCl (pH 3), and even less in water.

The relatively high melting point of metallic scandium, 1539° [9], its low specific gravity, considerable mechanical strength, and its low chemical activity under certain conditions are very valuable properties which make it a promising material for a number of areas of modern technology.

*V. A. Stepanov participated in the investigation.

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SORPTION OF GERMANIUM ON ALUMINUM HYDROXIDE

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Aluminum hydroxide is frequently used both in industry and in analytical chemistry [1] for the sorption of various substances. There are no data in the literature, however, on the sorption of microquantities of germanium by aluminum hydroxide. There is only a communication by Schwarz [2] on the preparation of aluminum germanate by mixing solutions of aluminum chloride and sodium germanate in the molar ratio $GeO_2 : Al_2O_3 = 3$ at pH 7. He showed that under these conditions the compound $Al_2O_3 \cdot 2GeO_2 \cdot nH_2O$ is formed. Sorption of GeO_2 on aluminum hydroxide also was studied by Schwarz with a large excess of GeO_2 in relation to the aluminum hydroxide, where the latter was used in the form of a dry powder; the pH was not checked. The maximum sorption (in relation to the initial amount of germanium) was 20%. In this connection it is known that the sorption of germanium by ferric hydroxide amounts to practically 100% [3, 4] and ferric germanate is insoluble [5].

The present communication presents results of investigations on the sorption of germanium present in solution in the form of germanic acid and the anion $HGeO_3^-$ [6] in relation to the concentration of germanium, the pH of the suspension, the temperature, and the time of contact of the precipitate with the solution. The aqueous solutions of germanium dioxide and ammonium sulfate used for the work were prepared from c. p. materials.

Ammonia or alkali was added dropwise to a mixture of solutions of germanium and aluminum. In this process a precipitate of aluminum hydroxide separated out, sorbing the germanium. The amount of coprecipitated germanium was calculated with respect to both the germanium content in the residual solution and the content of it in the hydroxide precipitate.

The solution and the hydroxide after dissolving in 4 N HCl were analyzed by the method of V. A. Nazarenko et al. [7]. An LP-5 potentiometer was used to measure the pH.

Experiments were first set up to determine the effect of the time of contact of the solution containing the germanium (14 mg/liter GeO_2) with the precipitate and of the temperature of precipitation at a weight ratio Al : Ge = = 100 and pH 7. It was established that when the time of contact was changed from 5 min to 48 hr and the temperature was changed from 20 to 80° (for 5 min contact) the sorption of germanium was 99% of the starting amount. All further experiments were set up at room temperature and the time of contact of the precipitate with the solution was 24 hr.

Figure 1 shows the effect of the pH of the suspension on the amount of germanium sorbed. It is seen that the maximum sorption was observed in the pH range from 6 to 9.6 (precipitation with ammonia), and complete precipitation of the aluminum hydroxide was reached at lower pH values than for germanium. With an increase in alkalinity the aluminum first started to dissolve. Thus at pH 9.6 about 20% of the aluminum dissolved, while practically no germanium went into solution. At pH 11 (precipitation with sodium hydroxide) 70% of the aluminum dissolved and only about 20% of the germanium. The isotherm for the sorption of germanium on aluminum hydroxide is represented on logarithmic coordinates in Fig. 2, and the relationship of the equilibrium concentration of germanium dioxide in solution to the molecular ratio $Al_2O_3 : GeO_2$ is shown in Fig. 3.

The deviation of the sorption curve from linearity (Fig. 2), the sharp breaks, and its large value (2.67 g of Ge per gram of Al) indicate the chemical nature of the sorption, i.e., sorption takes place as a result of the formation of insoluble aluminum germanates. The smooth development of the curve from the point of the first discontinuity (Fig. 2) and the increase in the equilibrium concentration of germanium (Fig. 3) with a decrease in the ratio $Al_2O_3 : GeO_2$ are explained by the fact that the precipitated aluminum germanates probably form solid solutions with the aluminum hydroxide. The equilibrium concentration of the germanium in the solution therefore depends on the amount of germanium sorbed by the aluminum hydroxide, i.e., on the concentration of germanate in the aluminum hydroxide.

With the molar ratio $Al_2O_3 : GeO_2 \approx 40$ (or 1 g Ge per 30 g Al) a saturated solid solution of germanate in aluminum hydroxide was formed and with a further decrease in the ratio $Al_2O_3 : GeO_2$ a solid phase of aluminum germanate itself appeared. From that moment on the equilibrium concentration of germanium in the solution did not depend on the ratio $Al_2O_3 : GeO_2$, i.e., on the amount of germanate separated out in the precipitate, but was determined only by the solubility of the germanate, which was ~0.32 mg/liter of GeO_2 (Figs. 2 and 3). This held true while there was sufficient aluminum for the formation of the difficultly soluble germanate. The second bend in the curve of Fig. 2 and the bend in the curve in Fig. 3 indicate an insufficiency of aluminum in relation to the stoichiometric amount of it in the germanate. As a result of this, the amount of germanium in solution starts to increase sharply in relation to the decrease in the ratio $Al_2O_3 : GeO_2$.

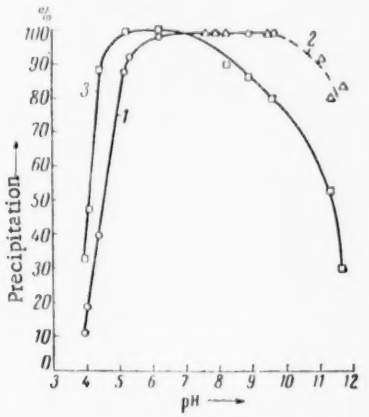

Fig. 1. Effect of pH on sorption of germanium by aluminum hydroxide. Concentration of GeO_2 14 mg/liter; Al : Ge = 100. 1) Percent sorption of germanium (precipitation with NH_4OH); 2) percent sorption of germanium (precipitation with NaOH); 3) percent precipitation of aluminum.

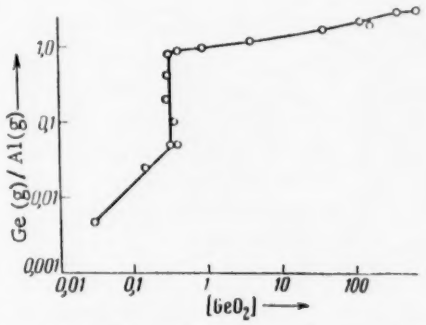

Fig. 2. Isotherm of sorption of germanium on aluminum hydroxide.

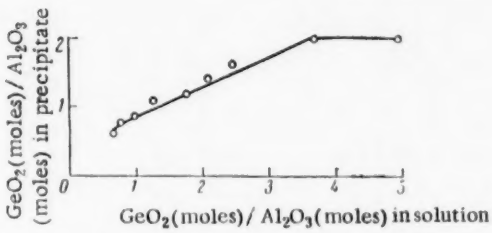

Fig. 4. Molar ratios $GeO_2 : Al_2O_3$ in the precipitate vs. starting ratios of these components in the solution.

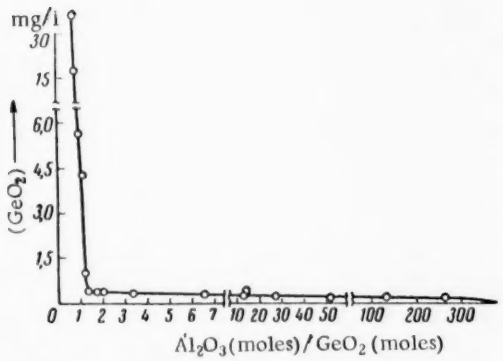

Fig. 3. Relation of equilibrium concentration of germanium in solution to the starting molar ratio $Al_2O_3 : GeO_2$.

Thus the ratio $Al_2O_3 : GeO_2$ at the point of flexion corresponds to their ratio in the most easily formed germanate. From Fig. 3 it is seen that this ratio is 1.5. Further sorption of germanium at $Al_2O_3 : GeO_2 < 1.5$ probably is explained by the formation of a more soluble germanate with a larger germanium content [2].

It appeared to us that the reaction proceeds according to the following equation:

$$1{,}5\ Al_2O_3 \cdot GeO_2 \cdot nH_2O + 2H_2GeO_3 \rightarrow$$

$$1{,}5\ Al_2O_3 \cdot 3GeO_2 \cdot m\,H_2O + q\,H_2O$$

and goes to completion only with a large excess of GeO_2 in the solution ($GeO_2 : Al_2O_3 > 3$, see Fig. 4).

Thus in order for the germanium present in solution at concentrations of less than 0.3 mg/liter to be sorbed it is necessary to use larger ratios Al_2O_3 : GeO_2 at which solid solutions are formed with a small concentration of germanate in the aluminum hydroxide.

Weight ratio Al:Ge	1	5	100	200	2000	5000	10000
Concentration of Ge, mg/liter	100	30	10	1	0.1	0.02	0.01
Precipitation of Ge, %	99	99	99	99	96	97	96

The data presented show that germanium can be precipitated practically completely on aluminum hydroxide [pH 7-8; 2% $(NH_4)_2SO_4$] even if the concentration of the former is 0.01 mg/liter. For this it is necessary to use a weight ratio Al:Ge = 10,000 (or M Al_2O_3 : M GeO_2 ≃ 13,000). For better coagulation of the hydroxide, it is necessary to add an electrolyte to the solution. It was established by numerous experiments that addition of such salts as NH_4Cl, $(NH_4)_2SO_4$, and NaCl as electrolytes has practically no effect on the sorption.

The conditions found by us for quantitative sorption of germanium by aluminum hydroxide at its greatest sorption capacity permit the proposal of a new gravimetric method for the determination of semimicro quantities of Ge (≃ 100 mg/liter) in solution. The determination can be made by precipitation with ammonia (pH ~7-8) of a known amount of aluminum from a pure solution and from a solution containing the germanium. In both cases the precipitate is filtered, washed, calcined, and weighted. The amount of the gain in weight in the second case corresponds to the germanium content in the sample solution.

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ACETATE COMPLEXES OF TITANIUM

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Kiev Polytechnic Institute

(Presented by Academician A. A. Grinberg, March 7, 1961)
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In colorimetric determinations of titanium with organic reagents and also in the study of the reaction in systems of titanium with organic complexing agents frequent use is made of acetate buffer mixtures. Most investigators do not take into consideration the possible reaction of titanium salts with acetate ions. Our experiments have shown that it is often impossible to ignore such reaction.

With large excesses of sodium acetate the titanium salts may be held in solution at pH 6 and above, while hydrochloric acid solutions of titanium at the same concentrations are hydrolyzed at pH 1-2. Furthermore, when a large excess of acetate ions is introduced the color is weakened in the colorimetric determination of titanium based on the formation of colored compounds with some organic reagents. All this can be explained by the existence of acetate complexes of titanium in which titanium is almost completely bound at pH's greater than 2.

We have studied the quantitative aspect of the reaction of titanium with acetate ions by precipitation of titanium in the presence of large excesses of sodium acetate.

The starting solutions were: a solution of titanium tetrachloride* in 2 N HCl (C_{Ti} = 0.19 M); a solution of analytically pure sodium acetate (C_{NaAc} = 1 M).

The experiments showed that when alkali was added to a solution of titanium in acetic acid the titanium was precipitated irreversibly, which apparently was connected with processes of change in composition and structure of the hydroxides [1]. Therefore the equilibrium pH value at which titanium started to precipitate was determined by us in the following manner The same amount of sodium acetate solution was added to several 50 ml flasks, then HCl was added in amounts calculated to give a range of pH values with an interval of 0.1-0.2 unit. After this the same volume of a solution of a titanium salt was added to each flask. The pH values of all the solutions were measured on a pH meter of the LP-5 system with a glass electrode. Furthermore, the optical density of the suspension was measured in an FEK N-54 photocolorimeter-nephelometer. A more precise value of the pH at the start of precipitation of the titanium was determined by extrapolation of the pH values obtained to zero value of the optical density. The experiments showed that equilibrium was established in 25-30 min after mixing the solutions. Although at this time titanium still continued to precipitate, the pH value of precipitation (found as described above) was practically unchanged. All the experiments were carried out at room temperature (22.0 ± 0.5°) and a constant ion strength μ = 0.5 (NaCL). The results of determinations of the pH values at the beginning of precipitation of the titanium salts were as follows:

Titanium concentration $\times 10^3$ M	3.82	3.82	3.82	3.82	3.82	5.30	5.20	3.04
Sodium acetate concentration	0.10	0.20	0.30	0.40	0.60	0.37	0.58	0.55
pH at start of precipitation of	2.22	2.35	2.57	3.03	3.93	3.69	4.40	4.55
titanium	2.22	2.35	2.57	3.03	3.93	3.69	4.40	4.55

Using these data, we attempted to determine the composition and stability of the acetate complexes of titanium. In this we proceeded from the fact that the titanium not bound in a complex is in solution in the form of titanyl ions (for example [2]), the concentration of which at pH values infinitely close to the pH for the start of precipitation is determined by the solubility product of titanyl hydroxide

$$SP = a_{TiO^{2+}} a^2_{OH^-} = 1 \cdot 10^{-30} \quad (^3).$$

* A solution of pure titanium tetrachloride was distilled over sodium amalgam and was subjected to two fractional distillations.

Assuming that complex formation proceeds by steps, we can calculate stability constants for the complexes $TiOAc^+$, $TiOAc_2$, etc.

$$\beta_1 = \frac{[TiOAc^+]}{[TiO^{2+}][Ac^-]}; \quad \beta_2 = \frac{[TiOAc_2]}{[TiO^{2+}][Ac^-]^2}$$

by Leden's method [4], the essence of which boils down to a graphical extrapolation of the functions $\Psi_1 = \Phi - 1/[Ac^-]$; $\Psi_2 = \Psi_1 - \beta_1/[Ac^-]$ etc. to zero concentration of the addend $[Ac^-]$.

Equil. Const. of Titanyl Ions $[TiO^{2+}]$	Conc. of acetate ions $[Ac^-]$	Degree of complexing Φ	Ψ_1	Ψ_2
$1{,}80 \cdot 10^{-5}$	$2{,}64 \cdot 10^{-4}$	$2{,}12 \cdot 10^{2}$	$7{,}7 \cdot 10^{5}$	$0{,}7 \cdot 10^{8}$
$6{,}60 \cdot 10^{-6}$	$7{,}15 \cdot 10^{-4}$	$5{,}80 \cdot 10^{2}$	$8{,}1 \cdot 10^{5}$	$0{,}8 \cdot 10^{8}$
$2{,}40 \cdot 10^{-6}$	$1{,}77 \cdot 10^{-3}$	$1{,}59 \cdot 10^{-3}$	$9{,}0 \cdot 10^{5}$	$0{,}8 \cdot 10^{8}$
$2{,}88 \cdot 10^{-7}$	$6{,}70 \cdot 10^{-3}$	$1{,}33 \cdot 10^{4}$	$1{,}9 \cdot 10^{6}$	$1{,}8 \cdot 10^{8}$
$4{,}56 \cdot 10^{-9}$	$7{,}20 \cdot 10^{-2}$	$8{,}40 \cdot 10^{5}$	$1{,}17 \cdot 10^{7}$	$1{,}52 \cdot 10^{8}$
$1{,}38 \cdot 10^{-8}$	$2{,}70 \cdot 10^{-2}$	$3{,}83 \cdot 10^{5}$	$1{,}43 \cdot 10^{7}$	$5{,}3 \cdot 10^{8}$
$5{,}60 \cdot 10^{-10}$	$1{,}64 \cdot 10^{-1}$	$0{,}95 \cdot 10^{-7}$	$5{,}70 \cdot 10^{7}$	$3{,}5 \cdot 10^{8}$
$2{,}62 \cdot 10^{-10}$	$1{,}97 \cdot 10^{-1}$	$1{,}16 \cdot 10^{7}$	$5{,}90 \cdot 10^{7}$	$3{,}0 \cdot 10^{8}$

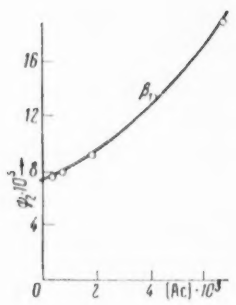

Fig. 1.

The degree of complex formation $\Phi = [Ti_{total}]/[TiO^{2+}]$, where $[Ti_{total}]$ is the starting concentration of titanium.

The equilibrium concentration of the titanyl ions can be determined from the equation

$$[TiO^{2+}] = \frac{SP}{\gamma_{TiO^{2+}} \cdot a^2_{OH^-}} = \frac{SP \cdot a^2_{H^+}}{\gamma_{TiO^{2+}} K_{H_2O}}.$$

The activity coefficient of the titanyl ion for ion strength $\mu = 0{,}5$ was calculated by us as for a bivalent ion in general according to the data in [5]. The value $\gamma_{TiO^{2+}} = 0{,}115$ was obtained. The ion product of water (K_{H_2}) for 22° and ionic strength $\mu = 0{,}5$ is $5{,}1 \cdot 10^{-15}$ [6].

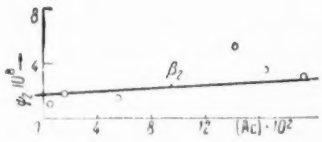

Fig. 2.

The acetate-ion concentration was determined from the equation

$$[Ac^-] = [NaAc] \frac{K_{HAc}}{[H^+] + [K_{HAc}]}.$$

The numerical values of the functions Ψ_1 and Ψ_2 are given in the table. The values of the stability constants β_1 and β_2 obtained were as follows:

$$\beta_1 = 7{,}5 \cdot 10^5; \qquad \beta_2 = 1{,}8 \cdot 10^8.$$

The instability constants of the acetate complexes will be:

$$K_1 = \frac{[TiO^{2+}][Ac^-]}{[TiOAc^+]} = 1 \cdot 10^{-6}; \qquad K_2 = \frac{[TiOAc^+][Ac^-]}{[TiOAc_2]} = 4 \cdot 10^{-3}.$$

The results obtained were used by us to explain some properties of titanium–phenol complexes. As our experiments showed, under certain conditions (pH 2-4) the reaction of titanium with o-polyphenols in the presence of acetate ions proceeds according to the scheme

$$TiOAc_x + nH_2R \rightleftarrows TiOR_n + xHAc + (2n - x)\,H^+$$

(charge signs omitted); H_2R is a diatomic phenol. At the same time at pH 1-2 acetic acid does not cause a change in color of phenol complexes ($K_p = [TiR_2][H^+]^2/[TiO^{2+}][H_2R]^2 = 10^{0.30}$)• and peroxide complexes of titanium

($K_p = [TiO \cdot H_2O_2^{2+}]/[TiO^{2+}][H_2O_2] = 10^{4.0}$) [7], although a calculation on the basis of the data that we obtained shows that under these conditions a considerable part of the titanium would be bound in colorless acetate complexes.

This discrepancy can be explained by the fact that in the determination of the stability of the peroxide and phenol complexes of titanium consideration was not given to the reaction of the latter with the anions of the inorganic acids (Cl^-, ClO_4^-, SO_4^{2-}) in the presence of which the determinations were carried out (there are, for example, data on the formation of complexes of titanium with ClO_4^- ions [2]). To explain what has been said above, we must assume that under these conditions (pH 1-2) at a NaCl concentration of 0.5 M the concentration of titanyl ions $[TiO^{2+}] \approx 10^{-3}[TiOCl_n]$, where $TiOCl_n$ are chloride complexes of unknown composition.

It has established that titanium salts form colorless complex compounds with acetic acid and its salts. At pH 2-3 the simplest complex $TiOAc^+$ is formed, and at higher pH values $TiOAc_2$ is formed. The instability constants calculated by the method of precipitation of titanium give the value $K_{TiOAc} = 1 \cdot 10^{-6}$ for the simplest complex and $K_{TiOAc_2} = 4 \cdot 10^{-3}$ for the more complex one.

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SYNTHESIS AND SOME TRANSFORMATION OF SILANES OF THE VINYLACETYLENE SERIES

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The most important and promising area of the chemistry of organosilicon compounds is that of the oxygen-containing compounds, among which the polyorganosiloxanes, silanols, and organosilicon alcohols are of especial interest.

In previous investigations we have described the synthesis and transformations of various organosilicon saturated and acetylenic alcohols [1] and silanols [2]. In the literature [3, 4] there are some indications of the reaction of Grignard reagents with polyorganosiloxanes, but there are no data on the reaction of polyorganosiloxanes with Iotsich's reagents. In this communication only the first results of a systematic study of the reactions of various Iotsich reagents with different polyorganosiloxanes are presented.

In the present investigation the reaction of a Iotsich reagent with polyorganosiloxanes was studied through the example of the reaction of vinylethynylmagnesium bromide with polydimethyl- and polydiethylsiloxanes:

$$CH_2=CH-C\equiv CMgBr + (RR'SiO)_x \rightarrow CH_2=CH-C\equiv C(R)_2SiOH,$$

where R and R' are the same or different radicals (H, CH_3, C_2H_5, etc.).

For evidence of the structure of the compounds obtained, the reverse synthesis of dimethylvinylethynylsilanol by saponification of dimethylvinyldiethylchlorosilane was carried out:

$$CH_2=CH-C\equiv C(CH_3)_2SiCl + NaOH \rightarrow CH_2=CH-C\equiv C(CH_3)_2SiOH + NaCl.$$

Thus two methods were found for the preparation of vinylethynylsilanols, which appear to be a new class of organosilicon compounds.

Dimethylvinylethynylchlorosilane was prepared by the reaction of vinylethynylmagnesium bromides with dimethyldichlorosilane:

$$CH_2=CH-C\equiv CMgBr + (CH_3)_2SiCl_2 \rightarrow CH_2=CH-C\equiv C(CH_3)_2SiCl + MgClBr.$$

Furthermore, the synthesis of dimethylvinylethynylchlorosilane was accomplished by us by the following scheme:

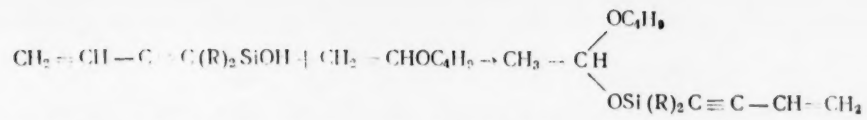
$$CH_2=CH-C\equiv C(CH_3)_2SiOH + SOCl_2 \rightarrow CH_2=CH-C\equiv C(CH_3)_2SiCl + SO_2 + HCl.$$

When thionyl chloride acted on dimethylvinylethynylsilanol, rupture of the Si–C bond was not observed.

Boiling vinylethynylsilanols in the presence of potassium carbonate, and also slow distillation of these compounds leads to their dehydration to the corresponding vinylethynyldisiloxanes

$$2CH_2=CH-C\equiv C(R)_2SiOH \rightarrow [CH_2=CH-C\equiv C(R)_2Si]_2O + H_2O.$$

Vinylethynylsilanes easily add to vinyl alkyl ethers in the presence of traces of concentrated hydrochloric acid with the formation of organosilicon acetals of the vinylacetylene series that have not been described in the literature.



Vinylethynylsilanols, chlorosilanes, disiloxanes, and acetals are easily polymerized. Their polymerization and copolymerization has been studied.

EXPERIMENTAL

Synthesis of dimethylvinylethynylsilanol. To the Iotsich reagent prepared from 163.5 g (1.5 moles) of ethyl bromide, 36.5 g (1.5 gram-atom) of magnesium in 400 ml of abs. ether, and 78 g (1.5 moles) of vinylacetylene was added, with heating on a water bath and stirring, 50 g of polydimethylsiloxane. The mixture was heated with stirring for another 10-12 hr. Then while the mixture was cooled carefully to 0° it was decomposed with 10% HCl and after the usual treatment 36.7 g (43.4%) of material was isolated with b. p. 56-57°/10 mm, $n^{20}D$ 1.4800, d^{20}_4 0.8943; MR found 40.09, calculated 38.00.

Found %: Si 22.43. $C_6H_{10}SiO$. Calculated %: Si 22.25.

In a similar manner ethylvinylethynylsilanol and diethylvinylethynylsilanol were prepared; their physicochemical constants are given in the table. The vinylethynylsilanols were colorless liquids with a carbinol odor, readily soluble in most organic solvents and poorly soluble in water. On storage in the light they turned yellow, gave off water, and polymerized.

Physicochemical Constants of Compounds Prepared

Expt. No.	Formula of compound	B. p., °C / mm Hg	n^{20}_D	d^{20}_4	MR found	MR calc.	Si, % found	Si, % calc.	Yield, %
1	$(CH_2=CH-C\equiv C)(CH_3)_2SiON$	56—57/10	1,4800	0,8943	40,09	38,00	22,43	22,25	43,4
2	$(CH_2=CH-C\equiv C)(C_2H_5)SiHOH$	64—65/22	1,4715	0,8960	39,41	39,26	22,55	22,25	23,2
3	$(CH_2=CH-C\equiv C)(C_2H_5)_2SiOH$	60—62/13	1,4875	0,9134	48,62	47,28	18,51	18,20	30,0
4	$(CH_2=CH-C\equiv C)(CH_3)_2SiCl$	53—54/26	1,4694	0,9570	42,15	41,72	19,23	19,42	53,4
5	$[(CH_2=CH-C\equiv C)(CH_3)_2Si]_2O$	98,5—100,5/12	1,4730	0,8911	73,80	72,54	24,21	23,96	33,3
6	$(CH_2=CH-C\equiv C)(CH_3)_2SiOCH(CH_3)OC_2H_7$	71,5—73/8	1,4504	0,8846	64,56	63,14	13,02	13,23	56,4
7	$(CH_2=CH-C\equiv C)(CH_3)_2SiOCH(CH_3)OC_4H_9-H$	111—113/26	1,4511	0,8819	69,12	67,77	12,37	12,41	32,9
8	$(CH_2=CH-C\equiv C)(C_2H_5)_2SiOCH(CH_3)OC_4H_9-H$	90—91/9	1,4558	0,8816	78,52	77,03	11,20	11,04	61,4

Synthesis of dimethylvinylethynylchlorosilane. In a 50 ml apparatus for synthesis were placed 19 g (0.15 mole) of freshly distilled dimethylvinylethynylsilanol and 1 g of pyridine. Then 26 g (0.21 mole) of thionyl chloride was added dropwise, with cooling and stirring. The mixture was stirred for 10 hr with cooling and for 12 hr with heating to 60°, and then was distilled in vacuum. Yield 11 g (53.4%) of material with b. p. 53-54°/26 mm, $n^{20}D$ 1.4694, d^{20}_4 0.9570; MR found 42.15, calculated 41.72.

Found %: Si 19.23. C_6H_9SiCl. Calculated %: Si 19.42.

Dimethylvinylethynylchlorosilane was prepared also by the reaction of vinylethynylmagnesium bromide with dimethyldichlorosilane in 19.4% yield.

Synthesis of dimethylvinylethynylsilanol. In a 0.5 liter apparatus for synthesis was placed 11.2 g (0.075 mole) of dimethylvinylethynylchlorosilane, two drops of phenolphthalein and 50 ml of abs. ether. The mixture was cooled to −5° and, while it was vigorously stirred, 0.25 N solution of NaOH was added to it until a lasting pale pink color appeared. The aqueous layer was separated from the ether layer and after the usual treatment of the latter 6.2 g (65.5%) of dimethylvinylethynylsilanol and 2.1 g (22%) of tetramethylbis(vinylethynyl)disiloxane were isolated.

Synthesis of tetramethylbis(vinylethynyl)disiloxane. In a 50 ml round-bottomed flask fitted with a reflux condenser were placed 35 g (0.28 mole) of dimethylvinylethynylsilanol and 5 g of calcined potassium carbonate. The mixture was heated at 80-90° for 1 hr, then cooled, filtered, and distilled in vacuum. On distillation we obtained

12 g of dimethylvinylethynylsilanol with b. p. 60-61°/12 mm, n_D^{20} 1.4780 and 11 g (33.3%) of tetramethylbis(vinylethynyl)disiloxane with b. p. 98.5-100.5°/12 mm, $n^{20}D$ 1.4730, d^{20}_4 0.8911; MR found 73.80, calculated 72.54.

Found %: Si 24.21. $C_{12}H_{18}Si_2O$. Calculated %: Si 23.96.

Synthesis of diethylvinylethynylsilylbutyl acetal. In an apparatus for synthesis was placed a mixture of 4 g (0.03 mole) of diethylvinylethynylsilanol and 3.0 g (0.03 mole) of vinyl butyl ether. Then one drop of conc. HCl was added with stirring. The temperature of the mixture rose sharply to 49°. To complete the reaction the mixture was heated for 1.5-2 hr more at 60-70°. Then the reaction mixture was neutralized with calcined potassium carbonate, filtered, and distilled in vacuum. On distillation 4.21 g (61.4%) of material with b. p. 90-91°/9 mm, $n^{20}D$ 1.4558, d^{20}_4 0.8816; MR found 78.52, calculated 77.03.

Found %: Si 11.20. $C_{14}H_{16}SiO_2$. Calculated %: Si 11.04.

In a similar manner dimethylvinylethynylsilylisopropyl acetal and dimethylvinylethynylbutyl acetal were prepared. The organosilicon vinylethynyl acetals were colorless liquids, soluble in organic solvents and insoluble in water, had a pleasant odor, and on long storage turned yellow and polymerized.

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RHENIUM AS A HYDROGENATION CATALYST

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Comparatively little work has been devoted to the investigation of the hydrogenation activity of rhenium. M. S. Platonov and co-workers [1] have shown that rhenium prepared by reduction of ammonium perrhenate at room temperature does not promote hydrogenation of a double bond (maleic acid, cyclohexene). This same conclusion may be reached from a consideration of the work of P. F. Ni and N. D. Sokol'skii [2]. However, in the colloidal state rhenium brings about hydrogenation of maleic and cinnamic acids at room temperature [3, 4]. An increase in the temperature to 250° leads to development of activity by rhenium with respect to hydrogenation of cyclohexene to cyclohexane. Benzene cannot be hydrogenated under these conditions, however.

Broadbent, Campbell, Bartley and Johnson [5] have carried out a detailed study of the hydrogenation activity of rhenium in which different classes of organic compounds were subjected to hydrogenation in the presence of rhenium "black" prepared by reduction of rhenium heptoxide. The hydrogenation was carried out in various solvents in an autoclave at 120-200° and an average hydrogen pressure of 150-200 atm.

Reduction of the Re_2O_7 was carried out both prior to and simultaneously with hydrogenation of the hydrogenatable substance. The authors showed that rhenium "black" is a good catalyst for reduction of carboxylic acids and their amides to alcohols and amines, respectively. The hydrogenation conditions included a temperature of 150-250° and a hydrogen pressure of the order of 200 atm. Double bonds, carbonyl groups, and nitro groups were hydrogenated in the presence of rhenium "black" at high temperature and pressure. The aromatic ring was reduced with difficulty; at 330° and 230 atm, only half of the benzene could be hydrogenated.

The hydrogenation activity of a catalyst prepared by reduction of a dioxane–rhenium heptoxide complex was studied in the present work. We have previously described the method of preparation of this catalyst, which we used in a study of dehydrogenation reactions, particularly the dehydrogenation of cyclohexane, a reaction for which rhenium was predicted to have activity by the multiplet theory.

In addition, we also prepared a skeletal rhenium catalyst by leaching a rhenium–aluminum alloy (containing 50% Re). The alloy was kindly given to us by our co-workers at the Institute of Metallurgy, Academy of Sciences USSR, M. A. Tylkina and K. B. Povarova, for which the authors express their appreciation. Hydrogenation of compounds containing a double bond, a carbonyl or carboxyl group, or an aromatic ring was studied with both catalysts.

EXPERIMENTAL

The Re/C catalysts were prepared by reduction of a dioxane–rhenium heptoxide complex deposited on activated carbon. The method of preparation has been described in [6, 7].

The skeletal rhenium catalyst, Re_{sk}, was prepared as follows. To a solution of 105 g of NaOH (c.p.) in 140 ml of water was gradually added, with stirring, 21 g of powdered rhenium–aluminum alloy. The reaction mixture was refluxed for an additional 30 min after completion of the reaction. The resulting catalyst was washed with water until free of base, as indicated testing with phenolphthalein; it was stored under water. The dried catalyst warmed somewhat on contact with air, but it was not pyrophoric. Colorimetric analysis of the catalyst, carried out in the manner described [8, 9], showed that the catalyst contained 86.5% metallic Re. Prior to use, the catalyst was washed several times with alcohol and the substance to be hydrogenated.

Experimental conditions. The majority of the experiments were carried out in a rotating autoclave with a column of 225 ml. In addition, experiments were carried out in a bomb and in a flow apparatus at atmospheric pressure.

The reaction products were analyzed chemically and by chromatography. The carbonyl compounds were separated and identified as the 2,4-dinitrophenylhydrazones and semicarbazones, and the alcohols were identified as the phenylurethans.

Hydrogenation of double bonds and carbonyl groups. Cyclohexene, octene, the dimethyl ester of maleic acid, benzene, and acetone were selected as objects of the investigation. The hydrogenation conditions and results are presented in Table 1. As may be seen from the table, hydrogenation of double bonds, aromatic bonds, and carbonyl groups is practically quantitative in the presence of the rhenium catalysts under rather vigorous conditions (high temperature and pressure). The hydrogenation of benzene over Re/C and Re_{sk} catalysts shows that these catalysts are different in this respect both from rhenium "black" and from the Platonov catalyst. In order to obtain a quantitative comparison of the rates of hydrogenation of a double bond and a carbonyl group, we investigated the hydrogenation of crotonaldehyde and of cinnamaldehyde in the presence of both catalysts. The hydrogenation was carried out as follows: the charge to the autoclave consisted of 20 ml of aldehyde, 50 ml of ethyl alcohol, and 0.7 g of catalyst. Samples were collected for analysis during the course of the hydrogenation. The hydrogenation temperature was 170-180°, and the initial hydrogen pressure was 110-130 atm.

TABLE 1. Hydrogenation in the Presence of Rhenium Catalysts

Substance hydrogenated	Amount, ml	Catalyst, g	Hydrogenation conditions			Hydrogenation product	Yield, %
			°C	init. press. H_2, atm.	time, hours		
Cyclohexene	20	Re/C 0,7	160	110	2	Cyclohexane	100
"	20	Re_{sk} 0,65	160	110	2	"	100
Octene	15	Re/C 0,7	180	100	2	n-Octane	100
"	15	Re_{sk}	180	100	2	"	100
Benzene*		Re/C	190	—	—	Cyclohexane	85
"	20	Re_{sk} 0,65	190	130	4	"	100
Acetone	20	Re/C 1	160	70	1	Isopropyl alcohol	100
"	20	Re_{sk} 0,65	160	100	1	" "	100
Dimethyl maleate**		Re_{sk}	20	1	10	Dimethyl succinate	100

* Hydrogenation in a flow system; volume of catalyst 36 ml; benzene feed rate 0.1 ml per min. The catalyzate obtained after one pass contained 85% cyclohexane.

** Hydrogenation in a bomb. Under these conditions Re/C does not promote hydrogenation of dimethyl maleate.

The results of the experiments are presented in Tables 2 and 3. It may be seen that in the presence of either catalyst, hydrogenation of the carbonyl group proceeded more rapidly than hydrogenation of the double bond both for crotonaldehyde and for cinnamaldehyde. In connection with this, it should be noted that unsaturated alcohol accumulated toward the end of the hydrogenation, and saturated aldehyde was absent. The data reported in [5] show that this selectivity is much greater in the case of rhenium "black;" the authors were able to obtain a hydrogenation product containing 94% crotyl alcohol.

Hydrogenation of carboxylic acids. Hydrogenation of acetic acid was carried out for 4-5 hr over Re/C catalyst at 200° and an initial hydrogen perssure of 120 atm. The product was a mixture of ethyl alcohol (20%), ethyl acetate (50%), and acetic acid (30%). An attempt to suppress the esterification reaction by addition of water led to a sharp decrease in the rate of hydrogenation and a decrease in the yield of hydrogenation products.

The Re_{sk} catalyst proved to be more active for the hydrogenation of acetic acid, which permitted a decrease in the reaction temperature. The hydrogenation product obtained at 170° and an initial hydrogen pressure of 120 atm was a mixture of 17.5% ethyl alcohol, 54.5% ethyl acetate, and 28% acetic acid. Hydrogenation of this mixture at 250° gave ethyl alcohol (83.4%) and ethyl acetate (16.6%).

Reduction of acetic anhydride in the presence of Re_{sk} catalyst at 150° and an initial hydrogen pressure of 145 atm gave a 60% yield of ethyl acetate.

TABLE 2. Hydrogenation of Cinnamaldehyde

H2/aldehyde (moles/mole)	Composition of hydrogenation product, wt. %			
	cinnamaldehyde	hydrogenated cinnamaldehyde	cinnamyl alcohol	hydrogenated cinnamyl alcohol
Re/C catalyst				
0,91	8,8	28,4	62,8	—
1,01	—	31,0	67,8	1,2
1,29	—	10,8	60,2	29,0
1,68	—	—	31,7	68,3
1,77	—	—	23,0	77,0
2,00	—	—	—	100
5,00*	Cyclohexylpropyl alcohol 100%			
Re_{sk} catalyst				
0,50	49,5	17,0	33,5	—
0,84	16,5	37,0	46,5	—
5,00*	Cyclohexylpropyl alcohol			

* The hydrogenation temperature was increased to 250°. Hydrogenation of the benzene ring was not detected at a lower temperature.

TABLE 3. Hydrogen of Crotonaldehyde

H2/aldehyde (moles/mole)	Composition of hydrogenation product, wt. %			
	crotonaldehyde	butyraldehyde	crotyl alcohol	butyl alcohol
Re_{sk} catalyst				
0,59	40,8	28,0	31,2	—
0,94	6,0	37,6	56,4	—
1,47	—	11,7	41,0	47,3
2,00	—	—	—	100
Re/C catalyst				
1,02	—	34,6	63,0	2,4
1,79	—	—	21,0	79
1,82	—	—	18,0	72

Propionic acid hydrogenated much more slowly than acetic acid; only 0.5 mole of hydrogen was absorbed per mole of propionic acid in 20 hr at 150°. An increase in the temperature to 250° lead to the absorption of an additional 0.5 mole of hydrogen in 5 hr. The hydrogenation product formed two layers; the catalyst was clumped in the lower layer. In all probability, this caused a decrease in the hydrogenation rate. The anhydrous hydrogenation product had the following composition (in wt. %): propyl propionate 59, propyl alcohol 8.7, and propionic acid 32.4. In order to prevent separation of the aqueous layer and clumping of the catalyst, the hydrogenation was carried out in the presence of ethyl alcohol, dioxane, and propionic anhydride. The results of the experiments are shown in Table 4. As would be expected, the hydrogenation rate increased sharply in the presence of the solvents, which prevented clumping of the catalyst. The best results were obtained when the hydrogenation was carried out in the presence of dioxane.

TABLE 4. Hydrogenation of Propionic Acid in the Presence of Re_{sk} Catalyst

Hydrogenation temp., °C	Initial press., atom.	H2/acid (moles/mole)	Hydrogenation time, hrs.	Solvent	Composition of water-free hydrogenation products, weight %		
					propyl alcohol	Propyl propionate	propionic acid
175	100	1,20	3	Dioxane	57,0	43,0	—
275	110	1,55	8	C_2H_5OH	64,2	Ethyl propionate 27,2 Ethyl acetate	3,4
170	110	1,9	4	Propionic anhydride	3,5	57,1	39,4
285	105	3,4	4		5,5	78,0	16,5

It has thus been shown that metallic rhenium supported on activated carbon and rhenium catalyst prepared by leaching rhenium–aluminum alloy are effective catalyst for the hydrogenation of double bonds, aromatic bonds, and carbonyl and carboxyl groups under pressure and at high temperatures.

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REDUCTION OF COPPER FERRITE, $CuFeO_2$, WITH GRAPHITE

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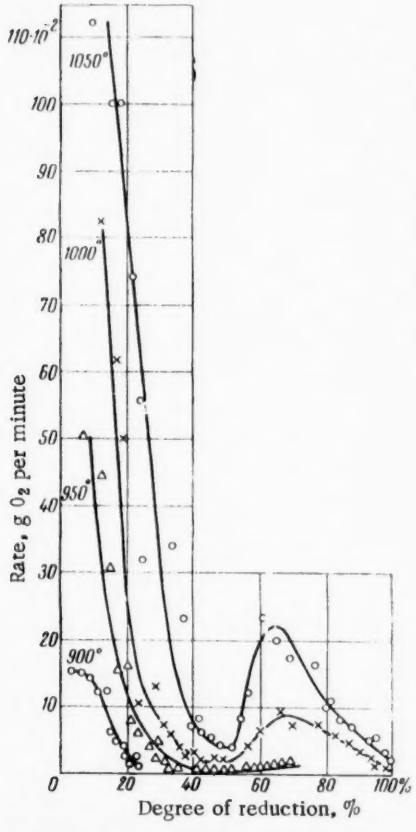
Copper ferrite in which the copper is monovalent has the composition $Cu^{1+}Fe^{3+}O_2^{2-}$ and a rhombohedral structure [1-3]. The kinetics of the reduction of this ferrite by graphite and the crystallochemical transformations occurring during the reduction were investigated in the present work.

The copper ferrite was prepared by sintering a mixture having the stoichiometric composition $Cu_2O + Fe_2O_3$ at 1000° in a stream of CO_2 for a period of 28 hr. X-ray investigation of the samples showed them to be single phase. Reduction by graphite was carried out under a reduced pressure of the order of 10^{-2} mm Hg. The reaction rate was determined from the weight increase of the sample measured over a specific time interval by means of a quartz spring balance. The rate was also determined by measuring the amount of carbon dioxide evolved over the same time interval; the carbon dioxide was collected by freezing it in a trap submerged in liquid nitrogen. A detailed description of the method is given in [4].



Reduction of $CuFeO_2$ by graphite at different temperatures.

The results of experiments on the kinetics or reduction at 900, 950, 1000 and 1050° are presented in the figure, from which it is seen that the reduction of copper ferrite was a stepwise process. At 900°, the process was complete at 25% reduction. Reduction was more extensive at the higher temperatures. The rate decreased initially, i.e., up to 50% reduction, after which it again increased. The kinetic curves have clearly expressed minimums and maximums.

The gaseous reaction products formed during reduction of $CuFeO_2$ by graphite are CO_2 and CO. In the initial stage, up to 33% reduction, carbon dioxide was practically the only component of the gas phase, and the ratio of CO to CO_2 became 1:1 at 50% reduction. The amount of carbon dioxide decreased gradually with further reduction.

The stepwise character of the reduction of copper ferrite was confirmed by x-ray structural analyses of the solid phases at different degrees of reduction.

Reduction, %	11	22	30
Phase	$CuFeO_2$, Cu, Fe_3O_4,	Fe_3O_4, Cu, $CuFeO_2$,	$CuFe_3O_4$, traces, $CuFeO_2$
Reduction, %	40	46	75
Phase	Cu, Fe_3O_4, FeO	Cu, FeO, Fe_3O_4	Cu, F FeO

In addition to the original ferrite, copper and magnetite (which gave a diffraction pattern characteristic of spinels) appeared at an early stage of the reduction. The original ferrite phase disappeared at 30% reduction, and wustite, formed by reduction of the magnetite, appeared at 40% reduction. After 50% of the oxygen had been removed, autocatalytic reduction of the wustite began, and copper, wustite, and iron were observed in the solid reaction products.

Ferrites, for which the mechanism of reduction has been studied earlier [4-6] had spinel structures and formed a continuous series of solid solutions with one of the reduction products – magnetite. Reduction of these ferrites by graphite at relatively high temperatures and low partial pressures of the reducing agent was accompanied by bulk diffusion of the metal ions in the solid phase. The ferrite formed by monovalent copper did not form solid solutions with magnetite, as shown by an investigation of the dependence of the equilibrium pressure of the oxygen in the gas phase on the degree of reduction. The results of this work will be published in detail later. The absence of mutual solubility of the original oxide and the products of its reduction suggest that the reduction of the ferrite formed by monovalent copper is not accompanied by appreciable bulk diffusion of the metal cations or of oxygen ions through the layer of solid reaction products. Surface diffusion plays an important part in this reduction. As a result, copper and magnetite crystals grow on the surface of the ferrite particles during reduction.

In our case, the samples were a powder of small particle size and the reduction took place at high temperatures and low partial pressures of the reducing agent, and the conversion of the ferrite to magnetite and copper was concluded before reduction of the magnetite began. Reduction of the magnetite proceeded as described in [7].

Thus, reduction of rhombohedral copper ferrite at 950, 1000, and 1050° proceeds in a stepwise manner with the formation of copper and magnetite in the first stage. Reduction of the magnetite through wustite to iron then takes place.

Analysis of our data shows that surface diffusion plays an essential part during reduction of the ferrite $CuFeO_2$ to magnetite and copper.

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THE STRUCTURES OF DIPHENYLCYCLOPROPENONE AND TROPONE SALTS

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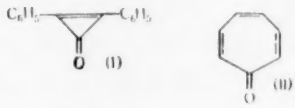
A characteristic feature of nonbenzenenoid aromatic ketones – diphenylcyclopropenone (I) and tropone (II) – is their ability to form salts with strong acids [1, 2].



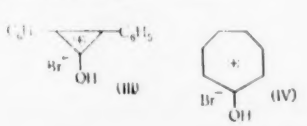
In order to clarify the structure of such salts, we synthesized the hydrobromides of diphenylcyclopropenone and tropone and investigated their infrared spectra.

Diphenylcyclopropenone was prepared by reacting tolane with dichlorocarbene [2]; it melted at 121-121.5°, and was purified by chromatographing on Al_2O_3. Anhydrous diphenylcyclopropenone hydrobromide was prepared by passing hydrogen bromide, dried over P_2O_5, into a solution of the ketone in absolute benzene. The resulting precipitate was quickly separated, washed with absolute benzene and petroleum ether, and dried over paraffin at atmospheric pressure with a brief pumping under vacuum toward the end of the drying. The salt melted at 121-121.5° (with decomposition). The substance was unstable. When heated or stored under vacuum, it split out hydrogen bromide with the formation of diphenylcyclopropenone. It was more stable in the form of the monohydrate $C_{15}H_{11}OBr \cdot \cdot H_2O$, m. p. 148.5-149° (with decomposition), to which it was converted on standing.

Tropone hydrobromide was prepared by passing dry hydrogen bromide into a solution of tropone in dry benzene. The precipitate was washed with benzene and dried in a manner similar to that used with the diphenylcyclopropenone salt.

The infared spectra of these salts in the crystalline state was characterized by the disappearance of the bands due to the carbonyl groups of the original ketones and the appearance of hydroxyl bands. Thus, the spectrum of diphenylcyclopropenone hydrobromide had no band at 1855 cm^{-1}, which is associated with valence vibrations of the C = O group in diphenylcyclopropenone [3]; there was also no band at 1621 cm^{-1}, a band which obviously must be considered as due to the valence vibration of the significantly localized double bond in the three-membered ring. In addition, the spectrum of the salt contained an intense broad band at 2976 cm^{-1}, which was undoubtedly due to the presence in the molecule of a hydroxyl group involved in the crystal structure by the formation of very stable hydrogen bonds. Bands which could be considered as characteristic of H–Br bonds (2300-2800 cm^{-1}) were not present in the spectrum.

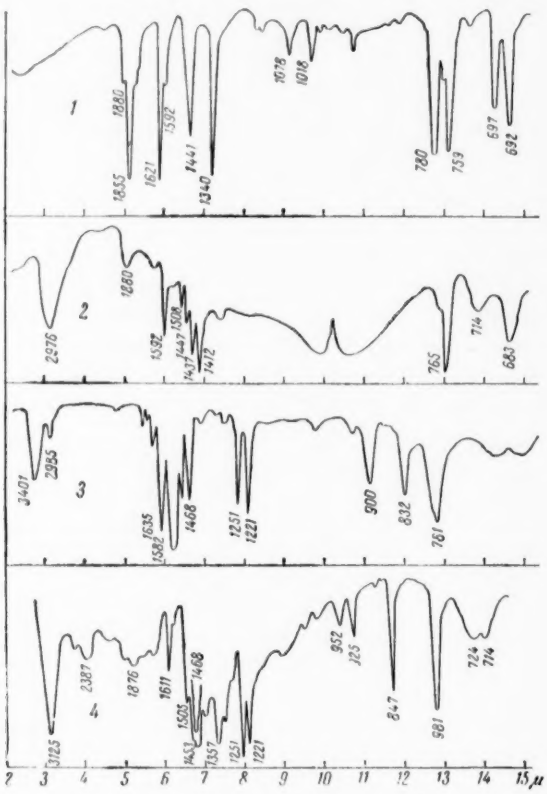
These data are in good agreement with the proposal that the salt has the structure (III); i.e., it is a salt of the nonbenzenoid aromatic diphenylhydroxycyclopropenylium cation.



The spectrum of tropone hydrobromide differed from the spectrum of the original tropone by the absence of a band at 1582 cm^{-1}, which is an intense band in the spectrum of tropone. This fact confirms the correctness of the assignment of this band to the carbonyl group of tropone, an assignment which was previously made in our paper [3] and in the paper of Borod'ko and Syrkin [4]. The band at 1635 cm^{-1} in the tropone spectrum, previously assumed to be a carbonyl band [1], is, in our opinion, due to vibrations of the double bonds in the ring; it is retained in the spectrum of the salt, but is slightly shifted to a lower frequency (1611 cm^{-1}), which is in complete agreement with the further equilization of the bonds in the ring during the transition from tropone to the hydroxytropylium ion. This is supported by the fact that in the Raman spectrum of the tropylium ion, $C_7H_7^+$, there is a band at 1594 cm^{-1}, which has been assigned to symmetrical vibrations of the aromatic ring [5].

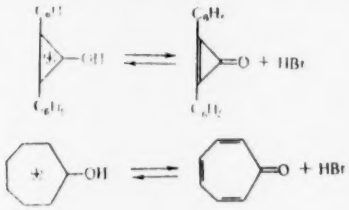
There was an intense band at 3125 cm^{-1} in the spectrum of the crystalline tropone salt. As in the case of diphenylhydroxycyclopropenylium bromide, this band undoubtedly indicates the presence in the molecule of a hydroxyl group. There were also in the spectrum two bands of average intensity at 2387 and 1876 cm^{-1}, which were apparently connected with the presence in the crystalline state of hydrogen bonds of the type O—H...Br. Assignment of these bands to H—Br bonds and, consequently, the presence in the solid salt of free hydrogen bromide are excluded by the absence in the spectrum of a band at 1582 cm^{-1}, which is characteristic of the free ketone.

All of these data persuasively show that this tropone salt has the structure (IV) and is a salt of the nonbenzenoid aromatic hydroxytropylium cation. Thus, the action of strong acids on diphenylcyclopropenone and on tropone proceeds with the addition of a proton to the carbonyl group, thereby converting it to a hydroxyl group, and the formation of the corresponding nonbenzenoid aromatic system.



I. r. spectra: diphenylcyclopropenone (1), diphenylhydroxycyclopropenylium bromide (2), tropone (3), hydroxytropylium bromide (4). 1, 2, 4) Crystalline state; 3) liquid.

This reaction is reversible; the action of a base on the salt results in the formation of the original ketone:



Cleavage of HBr from the salt also proceeds to a significant extent under the influence of a solvent.

The i.r. spectra of solutions of the salts in chloroform, dioxane, nitromethane, and other solvents showed bands characteristic of the original ketones (1855 and 1621 cm^{-1} for solutions of diphenylhydroxycyclopropenylium bromide and 1582 cm^{-1} for solutions of hydroxytropylium bromide). However, the intensities of these bands were somewhat lower than for the ketones themselves.

It is evident that the stability of these salts characterize the tendency of their ketones toward conversion from the partially delocalized system of π-electrons in the ring to a completely delocalized system of π-electrons with the formation of an aromatic system in the salts.

We also evaluated the instability constants of the salts in chloroform by means of data on the integral intensities of the carbonyl bands of solutions of the ketones and of their salts. According to our measurements, the integral intensities of the carbonyl bands of diphenylcyclopropenone and tropone in chloroform solutions were $5.9 \cdot 10^4$ mole·liter·sq cm and $3.5 \cdot 10^4$ mole·liter·sq cm, and the intensities of the carbonyl bands in the spectra of the salts of these ketones in equivalent solutions (at a concentration of $\sim 10^{-2}$ mole·liter) were $5.0 \cdot 10^4$ and $2.6 \cdot 10^4$ mole per liter·sq cm, respectively. Hence, the instability constant of diphenylhydroxycyclopropenylium bromide is $7.5 \cdot 10^{-2}$, and that of hydroxytropylium bromide is $1.8 \cdot 10^{-2}$.

Thus, tropone has a somewhat greater tendency toward the formation of a completely aromatic system of bonds than does diphenylcyclopropenone.

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THE MAGNETIC SUSCEPTIBILITY OF INNER-COMPLEX VANADYL COMPOUNDS WITH TRIDENTATE LIGANDS

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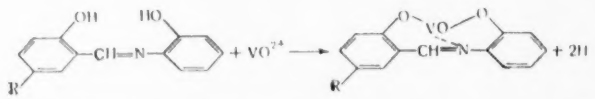
Magnetic data on inner-complex vanadyl compounds are very limited [1-5] owing to the fact that regardless of the stereochemistry of the complex, the magnetic moment is close to the value 1.73 μ_B, since in the ground state, $^2D_{3/2}$, tetravalent vanadium has one unpaired electron. Indeed, it has previously been shown that inner-complex vanadyl compounds with bidentate Schiff bases have magnetic moments very close to the spin-only value for a single unpaired electron. It has been proposed that these compounds are structurally tetragonal pyramids d^2sp^2 with the oxygen ion of the vanadyl group at the apex [5].

Certain deviations from the theoretical value of μ_{eff} are due to incomplete quenching out of the orbital component, and this, in the final analysis, depends on the nature of the ligand.

The study of vanadyl inner-complex compounds is also of interest from the point of view of the recent proposal by Bokii [6] to distinguish a special group of complexes in which the role of the ligand is played by an individual oxygen or nitrogen atom. The presence of different types of bonds is due to the fact that the number of ligands can vary for a given central atom.

We have previously shown that uranyl inner-complex compounds are, in this sense, analogs of the vanadyl complexes, since they also contain bonds of different types [7]. The uranium (VI) in these compounds exhibits a coordination number of six to eight, depending on the nature of the ligand. It is reported in the literature that vanadyl compounds also exhibit this same peculiarity. Thus, it has been shown that vanadyl hydroxyquinolinate adds a molecule of pyridine, thereby filling out the coordination number of tetravalent vanadium to six [3].

It seemed to us possible to prepare vanadyl compounds in which the vanadium has a coordination number of less than five, using for this purpose tridentate ligands, salicylal-o-hydroxyaniline, for example. Schiff bases of the type of silicylal-o-hydroxyaniline possess the peculiarity that they have two hydroxyl groups so disposed relative to the azomethine group that replacement of the hydrogen atoms by a divalent cation, vanadyl, for example, forms a very stable inner-complex compound containing one five-membered and one six-membered ring.



In this case, vanadium (IV) has an anomalous coordination number, similar to other transition elements, copper in particular [8, 9], and the compounds should possess peculiarities in properties in comparison with compounds in which vanadium has a coordination number of five or six. We proposed that these vanadyl inner-complex compounds should have an anomalously low paramagnetic susceptibility. We synthesized several vanadyl inner-complex compounds, and, as may be seen from the table, a study of their magnetic susceptibility at room temperature did indeed reveal that they have effective magnetic moments significantly lower than the spin-only value for a single electron.

The anomalous magnetic properties of vanadyl inner-complex compounds with tridentate ligands are apparently explained by the formation of metal–metal bonds.

The δ-bond arising between two vanadium atoms is formed as a result of partial overlap of the orbitals of two d electrons belonging to different vanadium atoms.

This leads to partial pairing of the electrons and, consequently, to a decrease in the effective moment. The observed slight increase in effective magnetic moment for vanadyl 5-chlorosalicylal-o-hydroxyanilinate (μ_{eff} = 1.32 μ_B) and vanadyl 5-bromosalicylal-o-hydroxyanilinate (μ_{eff} = 1.40 μ_B) over that of vanadyl salicylal-o-hydroxyanilinate (μ_{eff} = 1.19 μ_B) is apparently explained by the effect of the chlorine and bromine atoms. The replacement of hydrogen by chlorine and bromine increases the dimensions of the molecule of the inner-complex compound, and this, in turn, leads to a certain lengthening of the V–V δ-bond and, consequently, to an increase in paramagnetism as a result of the decrease in exchange interaction.

Compound	T, °K	$\chi_g \cdot 10^6$	$\chi_{ion} \cdot 10^6$	$\mu_{eff} \cdot \mu_B$
Vanadyl salicylal-o-hydroxyanilinate ($C_{13}H_9NO_2$)VO	291	1.73	652	1.24
Vanadyl 5-chlorosalicylal-o-hydroxyanilinate ($C_{13}H_9NO_2Cl$)VO	291	1.92	753	1.33
Vanadyl 5-bromosalicylal-o-hydroxyanilinate ($C_{13}H_8NO_2Br$)VO	292	2.00	914	1.47

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SEPARATION OF QUATERNARY ARSONIUM COMPOUNDS INTO OPTICALLY ACTIVE ANTIPODES BY ASYMMETRIC ADSORPTION ON NATURAL ASYMMETRIC ADSORBENTS

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The separation of unsymmetrical onium compounds into the optically active antipodes has usually been carried out by the classical method [1,4], which comprises the use of some optically active reagent with the formation of diastereoisomers, subsequent decomposition of these, and separation of the optically active component in accordance with the scheme:

$$l_1d_1 + d_2 \left\langle \begin{array}{l} \rightarrow l_1d_2 \rightarrow l_1 + d_2 \\ \rightarrow d_1d_2 \rightarrow d_1 + d_2 \end{array} \right.,$$

where l_1d_1 is the racemate under investigation, d_2 is the optically active reagent, l_1d_2 and d_1d_2 are a pair of diastereoisomers, and l_1 and d_1 are optical isomers of the substance investigated.

Since this method consists of three successive operations – formation of a pair of diastereoisomers, separation of this pair, decomposition of the pure diastereoisomer – it is difficult to carry out, and its effectiveness is low, particularly in the case where the diastereoisomers crystallize poorly or the optically active isomers have low stability. The latter probably explains the unsuccessful attempts of numerous investigators to resolve racemates.

In the present work, the separation of quaternary arsonium compounds was carried out by asymmetric adsorption on natural asymmetric adsorbents [5-7]. The separation of ethyl-n-amylphenylbenzylarsonium bromide was studied. This separation has previously been accomplished by the scheme described above [8], and it resulted in a compound with a rotation $[\alpha]^{20}D = +16.5°$.

It was, therefore, of interest to apply this new method to the separation of unsymmetrical arsonium compounds, on the one hand, and to confirm the previously obtained results, on the other.

The column employed in the experiments on the resolution of ethyl-n-amylphenylbenzylarsonium bromide racemic mixture was packed with dextrorotatory piezoquartz, which was prepared for use by grinding in a vibration mill in water (column diameter, 0.9 cm; adsorbent height, 23 cm; weight, 8.5 g; surface area, 28.1 sq m/g; 70% crystalline phase by x-ray determination). The separation was carried out as follows: a solution of 0.5 g of the compound in 1 ml of absolute alcohol was placed in the column and eluted with chloroform. When arsenic appeared in the eluate, fractions of 7 ml each were collected. The solution collected as the third fraction was found to have optical activity; the measurements gave: $[\alpha]^{20}D = +22.1°$ ($\alpha^{20}D = +0.24°$, $l = 1.9$). It was not possible to separate the levorotatory isomer in this case.

With the aim of separating the levo isomer, the experiment was repeated in a column packed with levoquartz (column diameter, 0.9 cm; absorbent height, 17 cm; weight of quartz, 6.5 g; surface area, 15.4 sq m/g). A solution of 0.3 g of ethyl-n-amylphenylbenzylarsonium bromide in 1 ml of absolute alcohol was passed through the column; chloroform was used as the eluent.

The third fraction, in which arsenic was present, was optically active: $[\alpha]^{20}D = -19.56°$ ($\alpha^{20}D = -0.09°$, $l = 1.9$).

Compound	Amt. of substance, g	Amt. of solvent, g	$\alpha^{20}D$, degrees	$[\alpha]^{20}D$, degrees	Tube length, dm
$\left[\begin{matrix} C_2H_5 & & C_6H_5 \\ & As & \\ C_5H_{11} & & C_7H_7 \end{matrix}\right]$ Br	0.0402	7	+0.24	+22.10	1.9
	0.0190	7	−0.09	−19.56	1.9

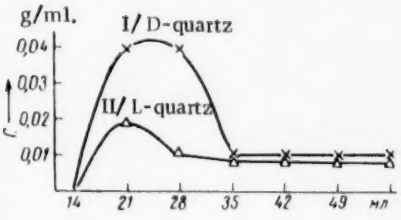

Fig. 1.

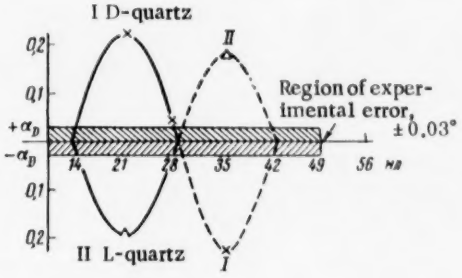

Fig. 2.

Further, from a consideration of the dependence of the concentration of the solution on the amount of fractions collected during the work with D- and L-quartz (Fig. 1), it is apparent that the concentration of one of the isomers increases and then decreases, while the concentration of the antipode is constant. Consequently, that it is impossible to separate both isomers when working with D- or L-quartz may be explained on the basis that the adsorption capacity of the active quartz is too great with respect to one of the isomers.

Consideration of the relationship between specific rotation of the solution and amount of fractions collected, as determined during the work with D- and L-quartz with the separation of isomers with $[\alpha]^{20}D = +22.10°$ and $[\alpha]^{20}D = -19.56°$, respectively (with the very low absolute divergence of 2.5°), persuaded us that if the quartz exhibits no great selective adsorption of one of the isomers, we should obtain both isomers with the same optical activity (Fig. 2).

Reliable results were not obtained when the ethyl-n-amylphenylbenzylarsonium bromide racemic mixture was resolved in a column packed with lactose. It should be noted that both the dextro and levo isomers resulting from separation in a column packed with optically active quartz changed into racemate within an hour.

Thus, the method of asymmetric adsorption on natural asymmetric adsorbents has been successfully used for the resolution of racemates of quaternary arsonium compounds; the first isomer isolated by this method was the levo isomer with $[\alpha]^{20}D = -19.56°$.

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THE MECHANISM OF THE FORMATION OF CARBONYL COMPOUNDS AND ACIDS DURING EMULSION OXIDATION OF ISOPROPYLBENZENE

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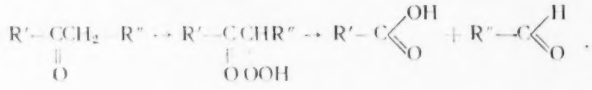
Carbonyl compounds arising during the course of oxidation of hydrocarbons, and which are also products of the further conversion of peroxides (or peroxide radicals), are formed by a radical mechanism in the majority of cases [1, 3]. Ketones and, in particular, aldehydes are very reactive compounds, and, therefore they readily become involved in a chain reaction yielding new substances with new functions. In particular, according to the scheme due to Rieche [4], the formation of acids proceeds by oxidation of ketones to α-ketohydroperoxides with subsequent decomposition of the latter to an acid and an aldehyde:



It is known that decomposition of α-ketohydroperoxides in accordance with the above scheme is catalyzed by acids [5]. This circumstance is evidently the reason why ketohydroperoxides have not been observed among the products of hydrocarbon oxidation. The route through dihydroperoxides [6] is a second possible mechanism for the formation of acids.

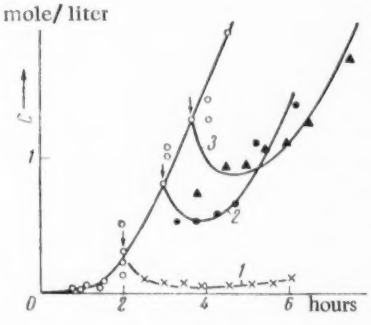


Fig. 1. Kinetic curves for the accumulation of peroxides during the oxidation of isopropylbenzene. 1,2) 0.15 mole/liter; 3) 0.03 mole/liter. Arrows indicate times at which inhibitor was introduced.

During a study of the oxidation of isopropylbenzene by the inhibitor method, we encountered a new and interesting phenomenon; when β-naphthol is introduced, the rate of formation of carbonyl compounds not only does not decrease, it increases abruptly. It seems to us that this sheds some light on the mechanism of formation of carbonyl compounds and acids during oxidation of hydrocarbons.

Emulsion oxidation of isopropylbenzene was carried out at a ratio of phases of 1:1 (the aqueous phase was an 0.1 N solution of sodium carbonate) in a thermostatted steel autoclave at a pressure of 10 atm and a temperature of 105°. Samples were collected during the course of the process and analyzed. Peroxides were determined iodometrically, carbonyl compounds were determined by the hydroxylamine method, and acids were determined by titration of the one phase. Inhibitor, β-naphthol, was introduced during the course of the reaction.

When inhibitor was introduced into the reaction mixture, the total amount of peroxides not only stopped increasing, but the peroxide concentration decreased (Fig. 1), which indicates that they are formed by a chain process and also that the consumption of peroxides compounds is by a molecular mechanism. Kinetic curves for the accumulation of carbonyl compounds are shown in Fig. 2. From the observed fact that the reaction is accelerated by the introduction of inhibitor it unequivocally follows that the formation of carbonyl compounds takes place by a molecular mechanism in this case, while consumption is by a radical chain mechanism. Vigorous consumption of carbonyl compounds began after the end of the inhibition period.

A break, but of a somewhat different character, is also observed on the kinetic curve for the formation of acids (Fig. 3). After the introduction of inhibitor, the concentration of acids sharply increased to a certain value, and then remained constant. This effect could be a consequence of the formation of acids from ketohydroperoxides. The inhibitor retarded the chain processes forming the hydroperoxides, and as a result the accumulation of acids continues until consumption of the ketohydroperoxides is complete and then stops. As the reaction emerges from the inhibition period, the formation of ketohydroperoxides again begins, and the decomposition of the ketohydroperoxides with the formation of acids and also the consumption of the acids set in. Since the concentration of ketohydroperoxides is initially small, these processes compensate each other, and this leads to a constant acid concentration over a length of time greater than the period of inhibition.

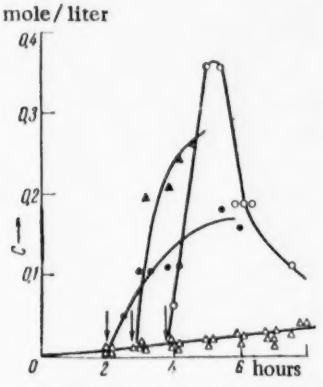


Fig. 2. Kinetic curves for the accumulation of carbonyl compounds during oxidation of isopropylbenzene. Arrows indicate the times at which inhibitor was introduced.

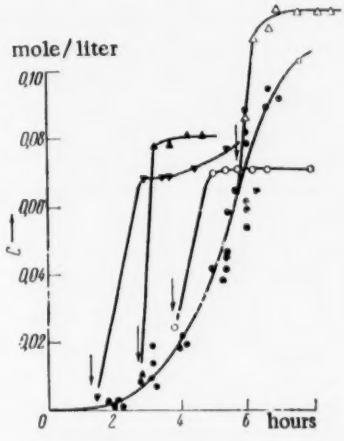
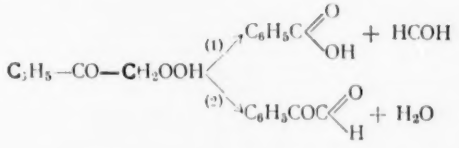


Fig. 3. Kinetic curves for the accumulation of acids during the oxidation of isopropylbenzene. Arrows indicate the times at which inhibitor was introduced.

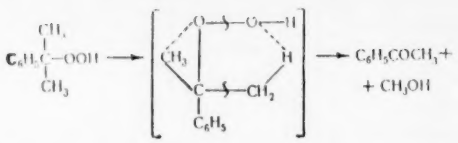
Extent of oxidation, C_{hp}, mole/liter	ΔC_{hp}, mole/liter	Tot. incr. of carbonyl and acids, ΔC, mole/liter	$\Delta C_{hp}/\Delta C$
0,3	0,25	0,24	1,04
0,8	0,34	0,33	1,03
1,25	0,43	0,425	1,01

According to Rieche's scheme, carbonyl and acid are formed in equivalent amounts during the decomposition of hydroperoxides (and even during the decomposition of dihydroperoxides). In the case of isopropylbenzene oxidation, the amount of carbonyl compounds formed during the period of inhibition of the reaction is several times greater than the amount of acid formed. It is natural to assume that the route of formation of carbonyl compounds during a single act of decomposition of ketohydroperoxide to acid and aldehyde is not unique. It is quite possible that the formation of carbonyl compounds and acids by the decomposition of ketohydroperoxides formed during oxidation of acetophenone takes place by the following mechanism:



The formation of phenylglyoxal by route (2) is quite possible. For example, methylglyoxal is formed during the oxidation of acetone, as has been shown by the work of E. T. Denisov [7].

A second possible route for the formation of carbonyl compounds is apparently molecular decomposition of cumene hydroperoxide:



For confirmation of the ideas proposed above, it is expedient to compare the consumption of hydroperoxide during the inhibition period with the overall formation of carbonyl compounds and acids. The appropriate data are presented in the table. We see that the amount of carbonyl compounds and acids formed during inhibition of the reaction is in good agreement with the amount of hydroperoxides decomposing by a molecular mechanism.

Thus, an intermediate compound (obviously, the α-ketohydroperoxide $C_6H_5COCH_2OOH$) appears kinetically during emulsion oxidation of isopropylbenzene, and this forms an acid and carbonyl compound by decomposition. This phenomenon cannot be detected during inhibition of oxidation processes taking place in homogeneous systems, since the formation of acids during the course of the reaction leads to a sharp decrease in the concentration of the intermediate hydroperoxide. In the case of oxidation in a weakly alkaline emulsion, the acid products in the aqueous phase are constantly neutralized (pH > 7), and the concentration of hydroperoxide can attain the values found by analysis, which, in our opinion, brings about the phenomenon under consideration.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

1,1'-BIS(ACYLPEROXY)DICYCLOHEXYL PEROXIDES

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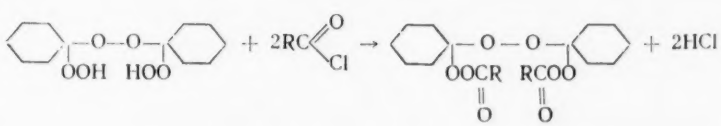
The action of hydrogen peroxide on cyclohexanone yields the so-called "cyclohexanone peroxide," an industrial product which is widely used as a polymerization initiator and as an initiator for other radical processes. This peroxide is a mixture of several peroxide compounds, and the relative amounts of the various peroxides in the mixture varies with the synthesis conditions. According to the data of Criegee [1], the mixture consists of 1,1'-bishydroxydicyclohexyl peroxide (I), 1-hydroxy-1'-hydroperoxydicyclohexyl peroxide (II), and 1,1'-bishydroperoxydicyclohexyl peroxide (III). Additional data on the synthesis, structure, and properties of I, II, and III are available in [2-4].

Information relative to acylation of I, II, and III is also available, but almost all of it relates to the acylation of II. Thus, the action of acyl chlorides on II in the presence of pyridine yields 1,1-bis(acyl)cyclohexyl peroxides [1, 5], $C_6H_{10}(OOCOR)_2$ (IV), where R is CH_3, C_6H_5, o-ClC_6H_4, p-BrC_6H_4, m-$NO_2C_6H_4$, p-$NO_2C_6H_4$.

As two of us have shown IV (with R = CH_3) is obtained in higher yield by the action of acetic anhydride on II in the presence of anhydrous sodium acetate [6].

With respect to acylation of I and III, it may only be remarked that when reacted with benzoyl chloride, I gives a small amount of benzoyl peroxide, and III forms 1,1'-bisbenzoylperoxydicyclohexyl peroxide [1]. The authors gave no indications of either the yields or properties of the latter compound.

It seemed to us to be of interest to investigate the reactions between III and acid chlorides and anhydrides with the aim of studying the possibility of synthesizing a new class of peroxy esters. We investigated the reaction of III with chlorides of acetic, propionic, n-butyric, n-capric, and chloroacetic acids in the presence of pyridine; we also studied the reaction of III with acetic anhydride in the presence of anhydrous sodium acetate. The reaction proceeds by the following scheme:



The yields of 1,1'-bis(acylperoxy)dicyclohexyl peroxides (V), calculated on III, were (in percent) 1,1'-bis(acetylperoxy)dicyclohexyl peroxide (Va), 78; 1,1'-bis(propionylperoxy)dicyclohexyl peroxide (Vb), 78; 1,1'-bis(butyrylperoxy)dicyclohexyl peroxide (Vc), 38; 1,1'-bis(caprylperoxy)dicyclohexyl peroxide (Vd), 59; 1,1'-bis(chloroacetylperoxy)dicyclohexyl peroxide (Ve), 38. The yield of Va from the reaction with acetic anhydride was 92% of theoretical.

All of these peroxides were solid crystalline substances with comparatively high melting points. They are stable during storage. The active oxygen content decreased somewhat on very prolonged storage. Thus, the activity of Vb decreased from 12.6 to 10.9 during storage for half a year, and the activity of Vc decreased from 11.5 to 10.4 in four months. With the exception of Vd, all of these peroxide compounds were sensitive to friction and shock; they exploded with great force. They are readily soluble in benzene and carbon tetrachloride and are somewhat less soluble in alcohol.

Infrared transmission spectra in the region covered by an IKS-14 spectrophotometer equipped with an NaCl prism were obtained for Va-Ve, III, and IV (R = CH_3).* The solutions investigated were 0.1 M with respect to peroxide, and the solvent was CCl_4. An 0.25 mm cell was used. The spectra are shown in Figs. 1 and 2.

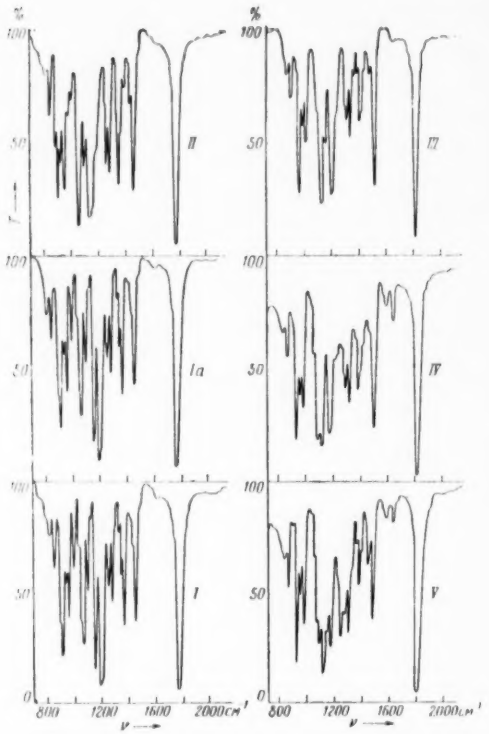


Fig. 1. Infrared transmission spectra of organic peroxides: I, Ia) 1,1'-bis(acetylperoxy)dicyclohexyl peroxide; II) 1,1'-bis(propionylperoxy)-dicyclohexyl peroxide; III) 1,1'-bis(butyrylperoxy)dicyclohexyl peroxide; IV) 1,1'-bis(caprylperoxy)dicyclohexyl peroxide; V) 1,1'-bis-(chloroacetylperoxy)dicyclohexyl peroxide.

Figure 1 (curve I and Ia) shows the infrared spectra of Va prepared by the two different methods. The spectra are identical. They differ from the spectrum of IV (R = CH_3), Fig. 2, curve II, in that the latter contains no band with a maximum at 930 cm^{-1} and also in that the intensities of the entire series of bands are significantly different.

For all of the peroxides, the spectra had a similar structure and possessed a series of characteristic bands. On the basis of the available experimental material and the literature data, a preliminary interpretation of the spectra is as follows.

The very intense band in the 1765-1800 cm^{-1} region is due to vibrations of the C=O group. In these spectra there is only one absorption band due to vibrations of the carbonyl group, while for diacyl peroxides this region of the spectrum has two bands assignable to C=O vibrations.

There was an intense band with a maximum at 1452-1455 cm^{-1} in all of the spectra. It is assigned to a scissoring mode of the CH_2 groups of the ring. Such an interpretation is in good agreement with the literature [7]. It is very difficult to identify bands in the spectra of complex compounds due to deformation vibrations of CH_3 and CH_2 groups in open chains in compounds containing both a ring and open chains, because the absorption bands of the ring and of these groups are superimposed. However, the band at 1350-1370 cm^{-1}, which is due to symmetrical deformation vibrations of the methyl group, is very stable if the methyl group is bonded to another carbon atom, especially a C=O group which has a very great effect on the stability of this band. This band, the interpretation of which cannot be doubted, is also observed in the spectra of Va-Vd (Fig. 1, curves I, II, III, and IV) and in the spectrum of IV (R = CH_3) (Fig. 2, curve II). Antisymmetric deformation vibrations of the methyl group at 1450-1455 cm^{-1} did not appear in the spectra, because in this region the scissoring mode of the CH_2 groups of the ring are superimposed on them, and the number of CH_2 groups is large in comparison to the number of CH_3 groups.

Two intense bands with maximums at 1195-1200 and 995-1000 cm^{-1} are observed only in the spectrum of Va (Fig. 1, curves I and Ia) and in the spectrum of IV (R = CH_3) (Fig. 2, curve II). Hence, it may be concluded that these frequencies should be assigned to vibrations of the $-\overset{\overset{O}{\|}}{C}-CH_3$ group at the end of a chain. The introduction of CH_2 and CH_2Cl groups changes the frequency of the vibrations and leads only to broadening of the adjacent bands.

A very intense band with its maximum at 1150-1160 cm^{-1} appeared in the spectra of all peroxides. In the literature [8], this band has been interpreted as a valence vibration of the $-\overset{\diagdown}{\underset{\diagup}{C}}-O$ bond in compounds containing hydroperoxy group, $-\overset{\diagdown}{\underset{\diagup}{C}}OOH$. That the spectra of the peroxides mentioned above would contain any sufficiently characteristic bands due to C–O vibrations is improbable. It is more natural to assume that the appearance of this band is connected with vibrations of the entire chain $-\overset{/\ \diagdown}{C}-O-O-\overset{\overset{O}{\|}}{C}-$ as a whole, and not just the C–O bond.

* The i.r. spectrum of IV was shown in [5]; however, only C=O group vibrations were studied.

Two bands with maximums in the 1097-1115 and 1065-1075 cm^{-1} regions should probably also be assigned to vibrations of this chain.

There are two weak absorption bands in the 830-900 cm^{-1} region of the spectrum. For compounds containing a hydroperoxy group, $-\overset{\diagdown}{\underset{\diagup}{C}}OOH$, the interpretation of bands in this region has been given in [9], where the band at 840 cm^{-1} was assigned to the short OOH chain, and the band at 880 cm^{-1} was assigned to O–O vibrations. It is hardly possible to expect O–O valence vibrations to appear in the infrared spectra of peroxides Va-Ve and IV (R = CH_3).

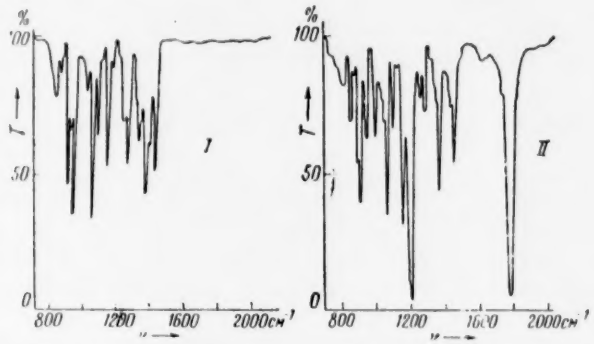


Fig. 2. I) 1,1'-bis(hydroperoxy)dicyclohexyl peroxide; II) 1,1-bis(acetyl)cyclohexyl peroxide.

EXPERIMENTAL

III was prepared by the method of [1]. The yield was 38.5%. M. p. 82-83°, mole wt.: found, 248 (benzene), calculated, 262.3.

Found %: C 55.54, 55.40; H 8.41, 8.86.* $C_{12}H_{22}O_6$. Calculated %: C 54.94; H 8.46.

Experimental method. The acyl chloride (0.03-0.06 mole) was added to a vigorously stirred solution of III (0.01-0.02 mole) in pyridine (0.05-0.1 mole). The reaction temperature was maintained within the range of −10 to 0°. After the addition of the acyl chloride, the reaction mixture was stirred for an additional 1-1.5 hr and was then discharged into cold water. The resulting precipitate was separated, washed 2-3 times with water, and recrystallized.

Va. The amount of III charged was 2.62 g (0.01 mole). There was obtained 2.7 g of Va (recrystallized from a mixture of alcohol and benzene). The yield was 78.0%. M. p. 78-78.5°. Mole wt.: found, 323.5 (benzene); calculated, 346.4. Active O: found, 13.5, 13.9; calculated, 13.8.**

Vb. The amount of III charged was 2.62 g (0.01 mole). There was obtained 2.93 g of Vb (recrystallized from a mixture of alcohol and benzene). The yield was 78.3%. M. p. 40-40.5°. Mole wt.: found, 334.1 (benzene); calculated 374.4. Active O: found, 12.4, 12.9; calculated, 12.8.

Found %: C 57.59, 57.40; H 8.23, 8.31. $C_{18}H_{30}O_8$. Calculated %: C 57.74; H 8.07.

Vc. The amount of III charged was 3.6 g (0.0137 mole). There was obtained 2.1 g of Vc (recrystallized from hot alcohol with subsequent cooling with ice). The yield was 38.1%. M. p. 52-52.5°. Mole wt.: found, 374.7 (benzene); calculated, 402.4. Active O: found, 11.2, 11.8; calculated, 11.9.

Found %: C 60.08, 59.70; H 8.40, 8.19. $C_{20}H_{34}O_8$. Calculated %: C 59.69; H 8.51.

Vd. The amount of III charged was 2.62 g (0.01 mole). There was obtained 3.38 g of Vd (recrystallized from a mixture of alcohol and benzene). The yield was 59.2%. M. p. 45-46°. Mole wt.: found, 515.5 (benzene); calculated, 570.7. Active O: found, 8.3, 8.2; calculated, 8.4.

Found %: C 67.18, 67.44; H 10.5, 10.2. $C_{32}H_{58}O_8$. Calculated %: C 67.35; H 10.24.

* The microsample was mixed with quartz sand prior to combustion. The authors thanks are due Z. M. Grabovskaya for carrying out the microanalyses.

** Determination of the active oxygen was carried out iodometrically in a manner similar to that described in [4].

Ve. The amount of III charged was 5.2 g (0.02 mole). There was obtained 3.2 g of Ve (recrystallized from a mixture of alcohol and benzene). The yield was 38.5%. M. p. 76.5° (with decomposition). Mole wt.: found, 383 (benzene); calculated, 415.3. Active O: found, 11.1; calculated, 11.5.

Found %: C 45.55, 45.70; H 6.46, 6.44; Cl 17.04, 16.71. $C_{16}H_{24}O_8Cl_2$. Calculated %: C 46.27; H 5.82; Cl 17.07.

Va. With acetic anhydride. To a mixture of 5 ml of acetic anhydride and 0.1 g of anhydrous sodium acetate was added, with vigorous stirring, 1 g of III. The reaction temperature, 31-32°, was maintained for a period of 2 hr, and 40 ml of cold water was then added. The precipitated crystals were separated, washed with water, and dried. Their weight was 1.22 g (92.4%); m. p. 77.5-78°. After recrystallization (alcohol–benzene), the crystals melted at 78-78.5°. A mixture of these crystals was Va prepared by the other route melted without depression of the melting point.

Found %: C 55.5, 55.27; H 7.97, 7.95. $C_{16}H_{26}O_8$. Calculated %: C 55.47; H 7.56.

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ON THE STRUCTURE OF δ-KETO ACIDS

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That γ-keto acids can react via two routes has long been known [1-3]. A cyclic, hydroxylactone structure has been demonstrated for certain of these acids by means of u.v. and i.r. spectroscopy [4-6]. Absorption bands due to cyclic forms have been found in the spectra of penicillic acid [4], acetophenone-o-carboxylic acids [5], and other acids of the same type [5, 6], while absorption bands due to open forms were absent. Recently, data have been obtained to show that δ-keto acids can undergo reaction via two paths [7, 8]. The formation of cyclic derivatives of keto acids can be due either to ring – chain tautomerism or to possible intramolecular cyclization of acyl cations formed during the course of the reaction from open-chain forms [9].

In this connection, it seemed of great interest to study the actual structures of δ-keto acids, which in the solid form have the structure of either keto acid (A) or hydroxylactone (B).

The i.r. spectra of a number of solid δ-keto acids (I-VII) and γ-bromo-α-keto acids (VIII-X) were studied in the present work along with the i.r. spectra of γ-p-tolylbutyronitrile (XI), hydrocinnamic acid (XII), and γ-phenyl butyric acid (XIII), which were selected as model compounds for the open form (A) of δ-keto acids.

δ-Keto acids I-III [10] were prepared by oxidation of the corresponding 1-alkyl-1-cyclopentanols. The remainder of the compounds were synthesized by previously developed methods and had melting points agreeing with those cited in the literature [11-14].

The i.r. spectra of these compounds were recorded in the 1800-600 cm^{-1} region with IKS-2 and IKS-12 instruments and in the 3600-2000 cm^{-1} region with an IKS-12 apparatus. Discs were pressed from mixtures of the compounds with potassium bromide (1-3 mg of the compound and 250 mg of potassium bromide). Spectra were also obtained from certain of the acids in vaseline oil, and no difference between these spectra and those obtained during the study with the discs was observed.

Typical curves from two of the ten acids investigated are shown in Fig. 1. All of the δ-keto acids (I-X) investigated gave intense absorption bands in the 3200-2600 cm^{-1} region; these were also observed with hydrocinnamic acid (XII) and γ-phenylbutyric acid (XIII), and are generally characteristic of acids (OH valence vibrations). A cyclic, hydroxylactone structure (B) of δ-keto acids should lead to the appearance of a single intense absorption band in the LiF region at 3400-3200 cm^{-1}, which is characteristic of lactones [4-6]. No such band was found.

All of the absorption bands characteristic of carboxylic acids in the 1800-600 cm^{-1} region were found, which permitted the unequivocal and persuasive conclusion that the solid δ-keto acids investigated have an open structure (A). The δ-keto acids studied in the present work absorbed intensely in the 1700, 1400, and 1300 cm^{-1} regions, which is characteristic of acids in the solid and in the liquid state [15].

δ-Keto acids I-III, VI, and VIII, in which the carbonyl group is not conjugated with the aromatic ring, had a single band in the 1700 cm^{-1} region; this band is associated with valence vibrations of ketone and carboxyl carbonyls.

In the case of δ-keto acids I-III and VI, this band lay in the interval 1712 ± 3 cm^{-1}. γ-Bromo-γ-acetylvaleric acid absorbed at 1735 cm^{-1}. δ-Keto acids V, VII, IX, and X, in which the ketone carbonyl group is conjugated with the aromatic ring, had bands in the 1700 cm^{-1} region at 1675 ± 5 and 1705 ± 10 cm^{-1}, the first of which corresponds to valence vibrations of a carbonyl group conjugated with an aromatic ring, and the second with valence vibrations of the C=O in a carboxyl group. γ-Benzoylbutyric acid (IV) absorbed at 1690 cm^{-1}.

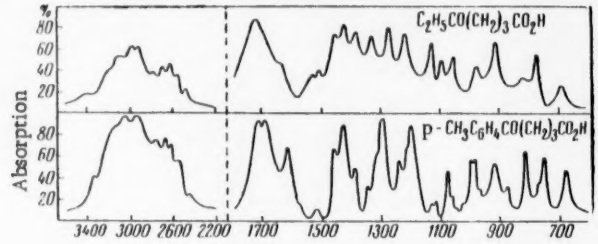

Fig. 1.

δ-Keto acid	R_1	R_2	R_3	M.p., °C	Lit. source
I	C_2H_5	H	H	47—48	[10]
II	C_3H_7	H	H	34—35	[10]
III	C_4H_9	H	H	42—43	[10]
IV	C_6H_5	H	H	127—128	[11]
V	p-$CH_3C_6H_4$	H	H	147—148	[12]
VI	CH_3	C_6H_5	H	47—48	[12]
VII	C_6H_5	CH_3	H	52—53	[12]
VIII	CH_3	CH_3	Br	74—75	[13]
IX	C_6H_5	H	Br	97—98	[11]
X	p-$CH_3C_6H_4$	H	Br	114—115	[14]

The band at 1420 ± 10 cm^{-1}, which was observed in the spectra of δ-keto acids I-X, is associated not only with the carboxyl group, but also with C—H deformation vibrations, the frequency of which is changed under the influence of neighboring ketone and carboxyl C=O groups. This is indicated by the greater-than-usual intensity of the band [16] and by the presence of absorption at 1421 cm^{-1} by γ-p-tolylbutyronitrile (XI).

An intense band in the 1300 cm^{-1} region, in the interval of 1303 to 1280 cm^{-1}, was found in the spectra of the δ-keto acids studied and also in the spectra of hydrocinnamic (XII) and γ-phenylbutyric (XIII) acids. The band was not present in the spectrum of γ-p-tolylbutyronitrile (XI), which proves a connection between this band and the carboxyl group.

As regards bands in the 900 cm^{-1} region, in spite of the limited correlation of bands in this region with structural factors [16], the acids investigated may be characterized by the following data: from one to three bands in the interval from 942 to 914 cm^{-1} were observed in the spectra of δ-keto acids I-X, while γ-p-tolylbutyronitrile (XI) did not absorb in this region; hydrocinnamic acid absorbed at 937 cm^{-1}, and γ-phenylbutyric acid absorbed at 917 cm^{-1}.

Thus, in the i.r. spectra of δ-keto acids I-X there are characteristic absorption bands associated with the carboxyl group, while absorption bands of lactols are absent, which proves that δ-keto acids have an open-chain structure (A).

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THE ADDITION OF TRIPHENYLMETHYL RADICALS TO ENYNE HYDROCARBONS AND SILICOHYDROCARBONS

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Only one case of the addition of stable free radicals to enyne hydrocarbons has been described. It has been shown that isopropenylacetylene adds triphenylmethyl radicals by 1,4-addition [1].

We have now established that other enyne hydrocarbons react with triphenylmethyl radicals by 1,4-addition with the formation of allenic hydrocarbons. Thus, an addition product with the composition $C_{43}H_{36}$ was obtained by the action of triphenylchloromethane and metallic mercury on vinylmethylacetylene (I). The i.r. spectrum of the product had a rather intense band at about 1960 cm^{-1} (Fig. 1, 1), which is characteristic of an allenic group, and bands characteristic of acetylenic and vinyl groups were absent. On the basis of these data, the product has been assigned the structure

$$(C_6H_5)_3C-\underset{\displaystyle CH_2}{\underset{|}{C}}=C=CH-CH_2-C(C_6H_5)_3.$$

In a similar manner, a 1,4-addition product was formed as a result of the addition of triphenylmethyl radicals to vinyl-tert-butylacetylene (II); however, we were unable to separate this product in the analytically pure form. The infrared spectrum of this addition product is shown in Fig. 1, 2.

In contrast to vinylacetylenic hydrocarbons, silicon-containing enynes add triphenylmethyl radicals in a different manner depending on the structure.

Vinyltrimethylsilylacetylene (1-trimethylsilyl-3-buten-1-yne, III) added radicals predominantly across the double bond. The i.r. spectrum of the product had an intense band at 2168 cm^{-1} due to the triple bond and a weak band in the region of 1945 cm^{-1}, where allenic compounds usually absorb (Fig. 1, 3).*

The structure of the addition product was confirmed by chemical means. Hydrolytic cleavage of the substance gave a hydrocarbon with a terminal acetylenic group in accordance with the reaction:

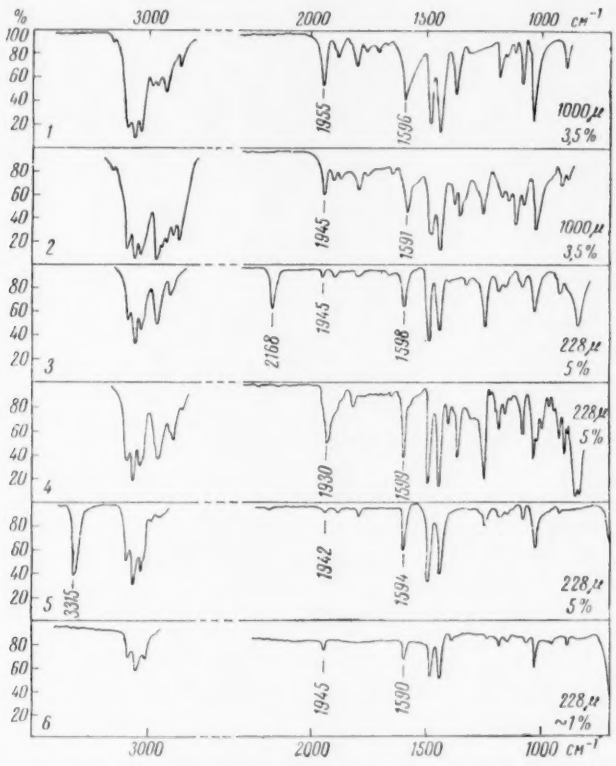
$$(CH_3)_3Si-C\equiv C-\underset{\displaystyle C(C_6H_5)_3}{\underset{|}{CH}}-CH_2-C(C_6H_5)_3 \rightarrow HC\equiv C-\underset{\displaystyle C(C_6H_5)_3}{\underset{|}{CH}}-CH_2-C(C_6H_5)_3.$$

The structure of the hydrocarbon was demonstrated by argentometric titration and by infrared spectroscopy; an intense band due to the terminal acetylenic group was found at 3315 cm^{-1} (Fig. 1, 5). In structure, this hydrocarbon is an isomer of the products obtained by 1,4-addition of triphenylmethyl radicals to vinylacetylene and was distinguished from it by having a higher melting point. Isopropenyltrimethylsilylacetylene (1-trimethylsilyl-3-methyl-3-buten-1-yne, IV) added triphenylmethyl radicals in the same manner as the enyne hydrocarbons, i.e., in the 1 and 4 positions. Triphenylmethane was formed as a by-product in this case.

The i.r. spectrum of the addition product had an intense allenic bond (1930 cm^{-1}), and bands attributable to an acetylenic bond were absent (Fig. 1, 4). Hydrolytic cleavage of the product gave an allenic hydrocarbon which has been described in the literature and which has previously been prepared by the addition of triphenylmethyl radicals to isopropenylacetylene [1]:

* It should be noted that detection of an acetylenic addition product was facilitated by the high intensity of the band due to valence vibrations of the tiple bond adjacent to a silicon atom.

The structure of the product of the addition of triphenylmethyl radicals to propenyltrimethylsilylacetylene (1-trimethylsilyl-3-penten-1-yne, (V) has not yet been reliably established. It apparently has a 1,3-diene structure, since its i.r. spectrum had no bands attributable to an allenic or acetylenic group; it is difficult for frequencies due to a 1,3-diene group to appear in the spectrum of a compound with six phenyl groups.



Infrared transmission spectra (of CCl_4 solutions): 1) 2-Methyl-1,-1,1,6,6,6-hexaphenyl-2,3-hexadiene; 2) 2-tertbutyl-1,1,1,6,6,6-hexaphenyl-2,3-hexadiene; 3) 1-trimethylsilyl-3-triphenylmethyl-5,5,5-triphenyl-1-pentyne; 4) 3-methyl-2-trimethylsilyl-1,1,1-6,6,6-hexaphenyl-2,3-hexadiene; 5) 3-triphenylmethyl-5,5,5-triphenyl-1-pentyne; 6) 4-methyl-1,1,1,6,6,6-hexaphenyl-2,3-hexadiene.

The difference in the course of the addition of triphenylmethyl radicals to a hydrocarbon (II) and a silicohydrocarbon (III) of analogous structure can be explained by the increase in steric hindrance at the acetylenic bond upon transition from a quaternary carbon to a quaternary silicon. In the case of the silicohydrocarbons (IV) and (V), steric hindrance also increased at the double bond, so that 1,4-addition became more favored. The lower yield of addition products and the presence of a side reaction – the formation of triphenylmethane – indicates a lower rate for the addition reaction in this case.

EXPERIMENTAL

The enyne hydrocarbons were prepared by alkylation of vinylacetylene [2],* and the silicohydrocarbons were prepared by the action of trimethylchlorosilane or organomagnesium derivatives of the corresponding enynes [3].

* The vinyl-tert-butylacetylene was prepared by I. A. Materina.

The experiments on the addition of triphenylmethyl radicals were carried out as follows. A mixture of triphenylchloromethane (m. p. 108-112°), the enyne compound (in excess), benzene, and metallic mercury (10 fold excess) was agitated in a hermetically sealed bottle in an atmosphere of inert gas for several days. The excess enyne compound and solvent were then distilled from the reaction products. The residue was extracted with ether. The oil remaining after distillation of the ether more or less rapidly crystallized on standing. The addition products were recrystallized from petroleum ether or acetone. All of the addition products were difficultly soluble in ether, petroleum ether, acetone, and carbon tetrachloride, and were practically insoluble in alcohol. The addition product obtained from silicohydrocarbon (V) was distinguished by particularly poor solubility. The constants an analytical data for all of the products are shown in the table.

Substance	M. p., °C	Yield, %	Found, %			Empirical formula	Calculated, %		
			C	H	Si		C	H	Si
$(C_6H_5)_2C-C\equiv C-CH(CH_3)-CH_2-C(C_6H_5)_3$	193—194	40	93,85 93,44	6,78 6,96	— —	$C_{42}H_{36}$	93,48	6,48	—
$(C_6H_5)_2C-C\equiv C-CH-CH_2-C(C_6H_5)_3$ $C(CH_3)_2$	150	53	91,42 91,31	7,63 7,63	— —	$C_{46}H_{42}$	92,93	7,07	—
$(CH_3)_3Si-C\equiv C-CH-CH_2-C(C_6H_5)_3$ $C(C_6H_5)_3$	178	62	88,53 88,21	7,00 6,87	4,53 4,27	$C_{43}H_{42}$	88,59	6,88	4,59
$(CH_3)_3Si-C\equiv C-C(CH_3)-CH_2-C(C_6H_5)_3$ $C(C_6H_5)_3$	128—130	27	88,59 88,39	7,24 7,17	4,54 4,67	$C_{44}H_{44}$	88,41	7,09	4,49
$(CH_3)_3Si-C\equiv CH-CH=C(CH_3)-C(C_6H_5)_3$ (?) $C(C_6H_5)_3$	161—161,5	50	88,65 88,57	7,30 7,29	4,58 4,67	$C_{44}H_{44}$	88,41	7,09	4,49
$HC\equiv C-CH-CH_2-C(C_6H_5)_3$ $C(C_6H_5)_3$	221	—	93,85 93,48	6,66 6,58	— —	$C_{42}H_{34}$	93,57	6,43	—
$(C_6H_5)_2C-CH=C-C-CH_2-C(C_6H_5)_3$ CH_3	184	—	—	—	—	$C_{43}H_{36}$	—	—	—

In the experiments with silicohydrocarbons (IV) and (V), triphenylmethane was separated in yields of 17 and 6%, respectively, from the residue remaining after evaporation of the ether. This product was distinguished from the addition products by considerably higher solubility in acetone and petroleum ether. The triphenylmethane melted at 93.5° (from petroleum ether). A mixture with a known sample showed no depression of the melting point.

Found %: C 93.48, 93.67; H 6.73, 6.90. $C_{19}H_{16}$. Calculated %: C 93.44; H 6.56.

Hydrolysis of the products of the addition of triphenylmethyl radicals to silicohydrocarbons (III) and (IV) was accomplished by refluxing for 35 hr with an alcoholic solution of KOH (25 fold excess). Recrystallization of the resulting hydrocarbons was from acetone or petroleum ether. The constants and analytical data for these compounds are shown in the table.

Argentometric titration [4] of the hydrocarbon obtained by hydrolysis of the addition product from silicohydrocarbon (III) gave 98.0 and 97.5% compound with a terminal acetylenic group.

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THE DECOMPOSITION OF CUMENE HYDROPEROXIDE CATALYZED BY KU-2 CATION-EXCHANGE RESIN

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It is well known that the acid form of cation-exchange resins can serve as catalysts for acid-catalyzed reactions. On the basis of this, we proposed that such catalysts would accelerate the decomposition of cumene hydroperoxide via an acid-catalyzed reaction mechanism. This proposal has been completely verified, as may be seen from the present communication, which contains the results of an investigation of the decomposition of cumene hydroperoxide in several solvents and in the presence of KU-2 cation-exchange resin.

The cumene hydroperoxide and the solvents were carefully purified, particular attention being given to the removal of traces of water. The KU-2 cation-exchange resin, which is a sulfonated copolymer of styrene and divinylbenzene, was ground and converted to the acid form by treatment with hydrochloric acid. The resin was then carefully washed and dried at room temperature. It was then ground again, and a fraction with a particle size of 0.3 to 0.4 mm was separated. Finally, the resin was given an additional drying at 90-95° under reduced pressure (about 1 mm Hg) for 25-30 hr.

The experimental method selected permitted us to carry out the experiments in a manner such that the catalyst, which was suspended in the solution, was distributed uniformly throughout the volume of the solution. Consequently, it could be assumed that there was a certain concentration, $\underline{m}$, of the heterogeneous catalyst in the reaction mixture.

The experimental method used in this work differed only in details from that described previously [1].

The solvents used in our study of cumene hydroperoxide decomposition catalyzed by cation-exchange resin KU-2 were acetone, dioxane, chlorobenzene, and glacial acetic acid; some mixed solvents were also used. The major products of the reaction were acetone and phenol, the yield of which reached 95-97% of theoretical. The KU-2 catalyzed decomposition of cumene hydroperoxide was autocatalytic in dioxane and in glacial acetic acid, while in acetone, chlorobenzene, and acetone–phenol and acetone–dioxane mixtures, the reaction was first order with respect to hydroperoxide up to the point at which the hydroperoxide concentration had decreased to 80-90% of its initial value. Deviation of this reaction from first order kinetics can be explained by the effect of the reaction products on the rate of the chemical reaction. In our experiments, the addition of acetone resulted in an increase in the reaction rate in all cases, while the addition of phenol brought about an increase, in some cases, and a decrease, in others, in the rate of decomposition of cumene hydroperoxide, the effect depending on the nature of the solvent. The results of some of these experiments are shown in Table 1, in which γ denotes the ratio of the maximum reaction rate in the presence of acetone, phenol, or a mixture of the two to the rate in the pure solvent.

The decomposition of cumene hydroperoxide at 30° in dioxane containing 2 moles/liter of acetone was 20 times as fast as in dioxane to which no acetone had been added. The acceleration of this reaction provided by the addition of phenol to the dioxane was altogether insignificant. The addition of equimolar amounts of acetone and phenol substantially accelerated the reaction.

If the effect of the end products of the catalytic decomposition of cumene hydroperoxide (CHP), i.e., acetone and phenol, on the reaction rate were insignificant, or if the effect were to decrease the rate, for example, by decreasing the initial hydroperoxide concentration, then the reaction rate, W, should be a linear function of hydroperoxide concentration C_{HP}.

$$W = k_e \cdot C_{HP} \qquad (1)$$

As the nature of the solvent was changed, there was a change in the manner in which the effective rate constant k_e of this reaction varied with a change in catalyst concentration. When the reaction was carried out in either aqueous or anhydrous dioxane or in glacial acetic acid, k_e was a linear function of the catalyst concentration, $\underline{m}$. Such a relationship between k_e and $\underline{m}$ indicates that all of the catalyst surface was uniformly available for adsorption of cumene hydroperoxide from the reaction mixture. When the reaction was carried out in acetone or chlorobenzene solution, the order of the reaction with respect to the catalyst was higher, 1.3-1.5. In our opinion, such a relationship between k_e and $\underline{m}$ is due to adsorption from the solution of impurities, water, for example, which greatly retard the acid-catalyzed decomposition of cumene hydroperoxide. In the case of water, such retardation has been observed both in the present investigation and in earlier work [2, 3] on the homogeneous decomposition of hydroperoxides.

TABLE 1. Catalyst concentration 5 g/liter

Solvent	Expt. temp. °C	Initial conc., moles/liter: hydroperoxide	acetone	phenol	γ
Chlorobenzene	50	0,1	0,1	—	2,3
	50	0,1	—	0,1	0,6
Acetone	30	0,1	90*	10*	3,7
	30	0,1	70*	30*	11,3
Dioxane	40	0,05	0,1	—	3,4
Chlorex	40	0,05	0,1	—	3,0
	40	0,05	—	0,1	1,2

* In mole percent.

The rate of cumene hydroperoxide decomposition catalyzed by KU-2 cation-exchange resin depended to a great extent on the nature of the solvent and on the natures of the several materials added. The results of the investigation of this quantitative relationship are presented in Table 2.

It is apparent from Table 2 that the decomposition of CHP was three or four times as fast in acetone as in dioxane. The reaction was especially slow in chlorobenzene. It was also established that the rate of the heterogeneous catalytic decomposition of cumene hydroperoxide was still lower in benzene than in chlorobenzene. The addition of phenol to acetone greatly accelerated this reaction, and the rate increase was greater the higher the phenol concentration. The addition of acetone and of an equimolar mixture of acetone and phenol to dioxane had an analogous effect. It was characteristic that at higher concentrations (above 0.5 mole/liter) of acetone in dioxane, acceleration of the reaction was the same as in the experiments in which an equimolar mixture of acetone and phenol was added. When the equimolar mixture of acetone and phenol was added to the dioxane at a concentration of the order of 0.1-0.2 mole/liter or less, the effect was less than when an equal amount of pure acetone was added.

The value of k_e for the reaction in dioxane increased linearly with an increase in the concentration of the equimolar mixture of acetone and phenol in the solvent. This made it possible to use graphical extrapolation to determine the value of k_e for the reaction in dioxane at a different temperature; such values are shown in Table 2. It is possible that these values differ somewhat from values determined directly from kinetic curves by the usual calculations. However, to calculate reliable values of k_e in these cases is difficult, since the reaction is autocatalytic, and the extent of autocatalysis is a complex function of the concentration of reaction products.

The addition of water to dioxane, even at comparatively low concentrations, considerably decreased the rate of decomposition of cumene hydroperoxide in the presence of KU-2 cation-exchange resin. A completely analogous effect of the addition of water has previously been observed in the sulfuric acid-catalyzed decomposition of CHP in dioxane [2, 3] and in glacial acetic acid [2].

The addition of 10 mole % benzene, toluene, meta- and paraxylene, or n-nonane to dioxane decreased to a comparatively small extent (by a factor of 1.2-1.5) the KU-2 resin-catalyzed decomposition of cumene hydroperoxide. It is characteristic that these additions did not eliminate autocatalysis. The extent to which the reaction was slowed by the addition of hydrocarbons increased with an increase in the molecular weight of the hydrocarbon, and there was absolutely no dependence on basicity of the hydrocarbon. Thus, for example, the addition of meta- or paraxylene decreased the rate of the catalytic decomposition of CHP to precisely the same extent, while, according to the data of reference [4], the basicity of metaxylene is 20-26 times greater than the basicity of paraxylene.

Values of the apparent activation energy, E, were calculated from the temperature dependence of k_e. The value of E varied with the nature of the solvent. Values of E were (in kcal/mole): 18.6 in acetone, 17.0 in a mixture of 90 mole % acetone and 10 mole % phenol, 15.5 in a mixture of 70 mole % acetone and 30 mole % phenol, 14.5 in dioxane and also in dioxane with additions of equimolar amounts of acetone and phenol, and 8.2 in chloro-

benzene with absolutely dry KU-2 resin and 12.2 with air-dried KU-2 resin. The value of the apparent activation energy calculated from the temperature dependence of the initial reaction rate in glacial acetic acid was 14.8 kcal per mole.

A comparison of values of k_e and E for reactions carried out in different solvents shows that the rate of the heterogeneous catalytic decomposition of cumene hydroperoxide is not determined solely by the value of E, but apparently also depends on a number of other factors including the specific adsorption of dissolved substances on the catalyst.

TABLE 2. Values of the Effective Reaction Rate Constant ($k_e \cdot 10^{-4}$ sec^{-1}) for the Catalytic Decomposition of Cumene Hydroperoxide as Functions of Temperature and Nature of the Solvent (catalyst concentration 5 g/liter)

Solvent	0°	10°	20°	30°	40°	50°	60°	70°	80°	90°
Acetone	0,1	0,37	1,18	3,25	7,85	—	—	—	—	—
90 mole % acetone + 10 mole % phenol	0,48	1,70	4,87	12,08	25,7	—	—	—	—	—
70 mole % acetone + 30 mole % phenol	2,06	6,51	16,22	37,06	—	—	—	—	—	—
Dioxane	—	—	0,4	1,0	2,0	4,1	—	—	—	—
Dioxane + 0.1 mole/liter acetone + 0.1 mole/liter phenol	—	—	0,4	—	2,35	4,85	—	—	—	—
Dioxane + 0.5 mole/liter acetone + 0.5 mole/liter phenol	—	—	0,8	1,7	4,6	7,9	—	—	—	—
Dioxane + 1.8 moles/liter acetone + 1.8 moles/liter phenol	—	—	1,5	3,3	7,3	17,6	—	—	—	—
95 mole % dioxane + 5 mole % water	—	—	—	—	—	—	—	0,2	—	—
Chlorobenzene *	—	—	—	—	0,09	0,16	0,27	0,42	0,79	1,25

* Concentration of air-dried catalyst was 25 g /liter.

In conclusion, the authors desire to express their appreciation to T. G. Brilkin, V. I. Ovechkina and N. V. Yablokov, who took part in carrying out the experiments in this investigation.

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A STUDY OF THE KINETICS OF THE ACID HYDROLYSIS OF CERTAIN PHENYL- AND CHLOROPHENYLGLYCOSIDES

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The study of the kinetics of acid hydrolysis of glycosides is of great interest. In particular, an answer to the question of what structural features of the sugar and the aglycon stabilize or activate glycoside bonds could serve to orient the development of routes for the directed synthesis of glycosides having a required stability of the glycoside bond, for example, during the formation of glycoside derivatives of medicinal agents.

The study of acid-catalyzed hydrolysis of glycosides has occupied numerous investigators, and there is now available information relating to the effect of the nature of the ring [1, 2], the configuration of the glycoside carbon atom [3, 4], and the configuration of asymmetric carbon atoms in the sugar residue [5]; data also exist on the effect of the nature of the aglycon and of different substituents in the aglycon [6-8]. However, comparatively little is known regarding hydrolysis of substituted phenylglycosides, and data on the hydrolysis of halogen-substituted phenylglycosides with different sugar components are completely absent.

In this connection, we undertook a study of the hydrolysis of phenylglycosides and halogen-substituted phenylglycosides of glucose, galactose, and xylose.

Glycosides containing the different sugar components and with chlorine substituted in the para position of the benzene ring were prepared for this purpose.

The method of synthesis of the phenylglycosides and the halogen-substituted phenylglycosides was based on the method of Helferich [9], which consists of three steps: 1) acetylation of the monosaccharide to obtain the acetyl derivative; 2) condensation of the acetate with phenol – preparation of the glycoside acetate; 3) saponification of the acetyl groups to obtain the free glycoside.

The most critical step is the second, since the first and third steps usually proceed with satisfactory yields. By modifying the second step of the reaction, we prepared the various acetylated phenylglycosides by convenient routes (see Table 1).

TABLE 1.

Compound	M. p., °C	$[\alpha]_D$ in water	Method of preparation
Phenyl-β-D-glucoside	174—175	—72,9	[11, 12]
Phenyl-β-D-galactoside	155—156	—42,3	[13]
Phenyl-β-D-xyloside	179—180	—50,8	[14]
p-Chlorophenyl-β-D-glucoside	173—174	—71,6	[14]
p-Chlorophenyl-β-D-galactoside	167—168	—47	[14]
p-Chlorophenyl-β-D-xyloside	153—154	—41	[15]

In the case of the phenylglycosides, saponification of the acetyl groups was carried out by the method of Pacsu [10].

The physical constants of the glycosides are shown in Table 1.

Owing to the difficulty involved in the synthesis of the glycosides, we used a semimicro polarimetric method to study the hydrolysis kinetics. This made it possible to carry out an experiment in which six to eight constants were determined with the use of only 0.21-0.25 g of material.

The hydrolysis was carried out with 1 N HCl at two temperatures, 60 and 80°. The temperature was maintained constant to within ± 0.05°.

The glycoside concentration was 2 to 3%. Samples of 0.5 ml were collected at different periods, and were neutralized with an equal volume of NaOH solution, the concentration of which very slightly exceeded 1 normal. Neutralization stopped the hydrolysis, and the very small excess of base eliminated errors which might arise as a result of mutarotation. After neutralization, the hydrolyzate was introduced into the semimicro polarimeter tube, which had a length of 1 dm and a volume of 0.8 ml.

TABLE 2

Parameter	0 min.	360 min.	540 min.	720 min.	840 min.	960 min.	1177 min.	∞
α	−1,77*	−0,54	−0,16	−0,09	+0,25	+0,40	+0,54	+0,91*
$K \cdot 10^3$, min.$^{-1}$	—	1,72	1,71	1,65	1,67	1,73	1,70	—

$$K_{cp} = (1,70 \pm 0,008) \cdot 10^{-3}$$

*Calculated.

TABLE 3

Compound	Hydrolysis temp., °C	K	t_h	E, kcal/mole
Phenyl-β-D-glucoside	60	$(1,70 \pm 0,008) \cdot 10^{-3}$	6 hr. 47 m.	29,86
	80	$(2,19 \pm 0,024) \cdot 10^{-2}$	52 m.	
Phenyl-β-D-galactoside	60	$(6,01 \pm 0,039) \cdot 10^{-3}$	1 hr. 55 m.	27,81
	80	$(6,51 \pm 0,133) \cdot 10^{-2}$	19 m.	
Phenyl-β-D-xyloside	60	$(1,99 \pm 0,048) \cdot 10^{-2}$	58 m.	27,24
	80	$(2,05 \pm 0,006) \cdot 10^{-1}$	6 m.	
p-Chlorophenyl-β-D-glucoside	60	$(1,29 \pm 0,016) \cdot 10^{-3}$	8 hr. 53 m.	28,73
	80	$(1,51 \pm 0,048) \cdot 10^{-2}$	77 m.	
p-Chlorophenyl-β-D-galactoside	60	$(4,51 \pm 0,070) \cdot 10^{-3}$	2 hr. 33 m.	27,30
	80	$(4,67 \pm 0,087) \cdot 10^{-2}$	25 m.	
p-Chlorophenyl-β-D-xyloside	60	$(1,84 \pm 0,035) \cdot 10^{-2}$	1 hr. 1 m.	26,57
	80	$(1,80 \pm 0,008) \cdot 10^{-1}$	6 m.	

The hydrolysis rate constants were calculated by the Arrhenius equation for first order reactions. The results of each experiment were checked by statistical treatment; the average probable error of the result was calculated. The calculated averages of the constants agreed for repeated experiments. Table 2 shows in somewhat more detail the data on the kinetics of the hydrolysis of phenyl-β-D-glucoside at 60°.

Since it is not possible to report in such great detail the experimental data for the hydrolysis of all of the glycosides at the different temperatures, we shall merely present the final results in the form of a condensed table (Table 3), in which the half-life periods (t_h) and the activation energies, E, are also shown. The probable error in calculating the constants was usually 1-2%.

A comparison of the hydrolysis of the glycosides leads to the following conclusions. The rate of hydrolysis of phenyl-β-D-galactoside at the two temperatures (60 and 80°) averaged three to four times higher than the rate of hydrolysis of phenyl-β-D-glucoside. Approximately the same ratio has been observed by other authors [16] in comparisons of the rates of hydrolysis of alkyl glycosides, although the latter hydrolyze considerably more slowly than phenylglycosides. Thus, a difference in configuration at the 4 carbon atom (glucose – galactose) has an appreciable effect on the stability of glycosides toward the action of acids.

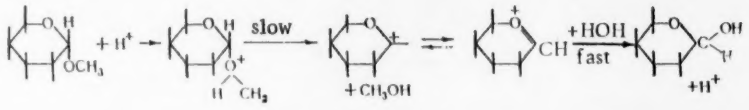
The rate of hydrolysis of phenyl-β-D-xyloside was approximately 10 to 12 times higher than the rate of hydrolysis of phenyl-β-D-glucoside under the same conditions. The xylosides and glucosides studied in these experiments have the same configuration of the first four asymmetric atoms, but they differ by the presence of a sixth carbon atom in glucose. Thus, this latter factor has a significantly greater effect on the hydrolysis rate than does configuration at the fourth carbon atom.

A halogen introduced into the para position of the benzene ring has much less effect on the rate of hydrolysis at both 60 and 80°, as may be seen by comparing the hydrolysis rate constants of the three pairs of glycosides.

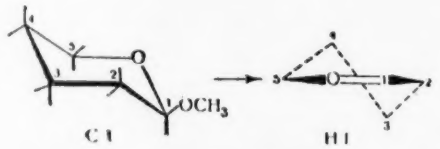
The activation energies for hydrolysis of the glycosides were close to 26-29 kcal/mole. The activation energies for the galactosides were somewhat lower than those for the glucosides, and those for the xylosides were somewhat lower than those for the galactosides.

These data on the relationship of hydrolysis rate to the sugar component are in good agreement with present concepts of the mechanism of acid hydrolysis and of the conformations of sugars [17], and, in turn, they represent new material confirming these concepts.

Of the two schemes of hydrolysis – Bunton [18] and Edward [19] – discussed in the literature in recent years, that of Edward apparently explains the greater number of facts (see also [20]). The scheme of Edward was developed predominantly for alkylglycosides:

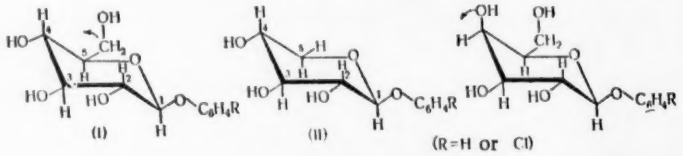


The usaturated oxonium ion exists in a half-chain, HI, conformation. The transition of a CI chair conformation, in which form the majority of pyranosides exist, to an HI conformation is accompanied by slight rotation of the atomic groups of the molecule around the 2,3 and 4,5 bonds.



Since the rate of hydrolysis is determined by the rate of the slow step – the rate of formation of the HI semi-chair form – factors affecting rotation of atomic groups around these bonds (2,3 and 4,5) are of great importance. For this reason it is indeed necessary to take into account the general positions associated with conversions of conformational forms: the bulky substituents attempt to occupy equitorial positions.

From this point of view, it is understandable that bulky substituents at C_5 must migrate to a position approaching axial, and such substituents will hinder rotation, i.e., slow down hydrolysis. This apparently explains the low hydrolysis rate of glucosides (I) as compared to that of xylosides (II) in our experiments.



In addition, the hydroxyl at C_4 which is in an axial position in the galactosides (III) will approach an equitorial position during the rotation in the transition to the half-chair form HI, and this accelerates hydrolysis of galactosides as compared to hydrolysis of glucosides.

It is impossible not to note that our data do not contradict the scheme postulated by Bunton [18] for hydrolysis of glycosides, according to which hydrolysis is preceeded by opening of the ring of the sugar component. In this connection, it should be mentioned that earlier, during a study of the content of open forms of various sugars in solution [21], we arranged the sugars in the following order with respect to decreasing content of the oxo form: glucose > galactose > xylose; i.e., this series agrees completely with the series of the corresponding glycosides.

With regard to the effect of substituents in the aromatic aglycon on the hydrolysis rate of glycosides, the following may be noted. Some information is available in the literature to the effect that orienting groups of the first order, for example, methyl, butyl, and propyl, increase the rate of hydrolysis [7]; in previously published work it was shown that the hydroxyl in arbutin increases the hydrolysis rate by a factor of two over that of the phenylglucoside [22].

It is well known that halogens behave peculiarly as orienting groups; they are orienting groups of the first order, but, in addition, they decrease the electron density in the ring.

The somewhat slower hydrolysis of the three p-chlorophenyl-β-D-glycosides as compared to the hydrolysis rates of the phenylglycosides, as observed in our experiments, is apparently explained by a decrease in the electron density in the ring, which hinders the addition of a proton to the oxygen of the glycoside bond.

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MOLYBDENUM AND RHENIUM DISELENIDES

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$MoSe_2$ was first prepared by heating molybdic acid with selenium in a stream of hydrogen [1], and $ReSe_2$ was first prepared by decomposition of Re_2Se_7 at 325-330° under vacuum [2]. Judging from the literature, the crystallochemical and electrical properties of these compounds have not previously been studied. Inasmuch as molybdenum and rhenium disulfides [3] have the same type of crystal structure and MoS_2 is a known semiconductor, it appeared to be of interest to study the properties of molybdenum and rhenium diselenides from this point of view.

The synthesis of $MoSe_2$ and $ReSe_2$ in the present work was carried out by sintering powdered molybdenum or rhenium (both of about 99% purity) with the stoichiometric amount of selenium (99.9% selenium) in quartz ampoules (which had been sealed under vacuum) at 700° for 100 hr. The resulting preparations were gray powders with a metallic luster and were completely stable in air. X-ray photographs of the samples were taken with RKD-57-type cameras using copper radiation. The table presents the results obtained from the powder pattern of $MoSe_2$. Molybdenum diselenide has a hexagonal unit cell with the parameters: a = 3.28_4 kX; c = 12.8_8 kX.

Indices from Powder Pattern of $MoSe_2$; Cu $K\alpha$ = 1.539 kX

Intensity	$\sin^2\theta \cdot 10^4$ found	*hkl*	$\sin^2\theta \cdot 10^4$ calc.	Intensity	$\sin^2\theta \cdot 10^4$ found	*hkl*	$\sin^2\theta \cdot 10^4$ calculated
8	140	002	143	5	3496	204	3499
2	565	004	571	3 b	3833	205	3820
8	732	100	732	7	4486	118	4479
1	870	102	875	2	5131	120	5124
10	1058	103	1053			0012	5138
4	1284	006	1284	6	5445	123	5445
6	1628	105	1624	1	5757	1110	5764
10	2197	110	2196	3 b	6014	125	6016
5	2284	008	2283	4	6586	300	6588
4	2342	112	2339	1	6718	302	6731
2	2771	114	2767	3	7875	306	7872
4	2934	200	2928	4 b	8780	220	8784
6	3249	203	3249	5	8878	308	8871

The pycnometric density of $MoSe_2$ was found to be 6.90 ± 0.05 g/cc.

If it is assumed that, like the MoS_2 unit cell, the $MoSe_2$ unit cell contains two formula units, the calculated density of $MoSe_2$ is found to be 7.0 g/cc, which is in good agreement with the density found experimentally. The majority of the lines in the $MoSe_2$ powder pattern indexed with the same *hkl* indices as the lines in the MoS_2 powder pattern. Moreover, in the two cases the conditions for nonabsorption of reflections of the types *hhl* and *00l* for even *l* were the same. All of this suggests that molybdenum diselenide and disulfide are isostructural compounds.

The $ReSe_2$ powder pattern had its own set of interplanar distances, which indicates that the reaction between rhenium and selenium was complete. It contained a considerably greater number of lines than did the powder pattern of $MoSe_2$, and these could not be fitted to a unit cell of the MoS_2 type. It is probable that the structure of molybdenum diselenide has a lower symmetry.

The electrical conductivity and thermal emf of $MoSe_2$ and $ReSe_2$ were measured potentiometrically by a compensation method.* The samples were rods having a diameter of 4 mm and a length of 12-15 mm. These were passed from the powders under a pressure of 8 tons** /sq cm. The electrical conductivity was measured over a temperature range of 20-70°. The specific electrical conductivity of $MoSe_2$ at 22° was $1.23 \cdot 10^{-4}$ $ohm^{-1} \cdot cm^{-1}$, with an increase in the temperature of the sample, the conductivity increased appreciably, and at 62° it was $2.30 \cdot 10^{-4}$ $ohm^{-1} \cdot cm^{-1}$. For $ReSe_2$ at 24° it was 6.75 $ohm^{-1} \cdot cm^{-1}$, and at 64° it had increased to $10.7 \cdot 10^{-5}$ $ohm^{-1} \cdot cm^{-1}$. The positive temperature coefficient of the electrical conductivity and its value indicate semiconductor properties for $MoSe_2$ and $ReSe_2$, and this was confirmed by the high thermal emf which we observed for these compounds. The thermoelectromotive force of the $MoSe_2$ and $ReSe_2$ samples was measured by an integral method [5] with respect to alumel. The temperature difference between the ends of the sample was varied from 25 to 150°. The thermal emf of $MoSe_2$ under these conditions varied in the interval 610-430 μv/degree, respectively, while that of $ReSe_2$ varied from 1200 to 800 μv/degree. In both cases, the hot probe (alumel) was charged negatively, whence it may be assumed that our samples of molybdenum and rhenium diselenides were p-type semiconductors [5].

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* We have described the method of measurement in [4].

** The Russian ton is 2203 pounds – Publisher.

INVESTIGATIONS IN THE FIELD OF THE SYNTHESIS AND REACTIONS OF UNSATURATED ORGANOSILICON COMPOUNDS

THE SYNTHESIS OF BRANCHED SILICOHYDROCARBONS OF THE DIACETYLENE SERIES

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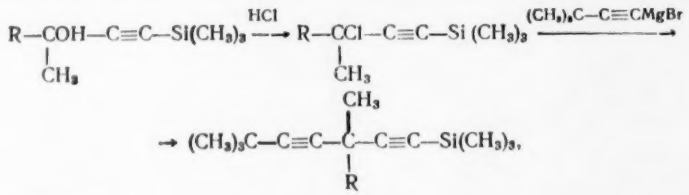
In our preceding investigations, we have studied the synthesis and reactivity of organosilicon acetylenic and diacetylenic alcohols [1] and of silicohydrocarbons of the vinylacetylene series [2].

Studies carried out in connection with the further development of our investigations led to a new method of synthesis of branched diacetylenic silicohydrocarbons, which is described in the present paper. This method is based on halogen derivatives of organosilicon acetylenic alcohols and tertiarybutylacetylene according to the scheme



where R = CH_3, C_2H_5, or tert-C_4H_9.

The presence of two triple bonds in the resulting diacetylenic silicohydrocarbons was proved by hydrogenation to the saturated compounds. As a result of our investigations, we have prepared and characterized, for the first time, three representatives of organosilicon acetylenic chlorides [1-3] and three representatives of branched diacetylenic silicohydrocarbons [4-6], the constants of which are presented in the table.

EXPERIMENTAL

In the synthesis of the acetylenic chlorides, the reactions were carried out in a three-neck, round-bottom flask having a volume of 150 ml and fitted with a reflux condenser and thermometer.

Synthesis of 5-trimethylsilyl-3-methyl-3-chloro-4-pentyne (1). Gaseous hydrogen chloride was passed into a reaction flask containing 21.25 g of 5-trimethylsilyl-3-methyl-4-pentyne-3-ol (b. p. 61-62°/2 mm) at 30°. This caused the temperature of the reaction mixture to increase to 48°. Two layers formed in the flask over a period of 45 min, and the reaction was stopped. The upper layer was separated from the lower (aqueous) layer, dried with $CaCl_2$, and distilled under vacuum. This yielded 15 g (63.8%) of 5-trimethylsilyl-3-methyl-3-chloro-4-pentyne with a b. p. of 38-40° (2 mm). Two other representatives of acetylenic monochlorides of different structure were prepared by this method. The constants of all three of these chlorides are shown in the table.

Synthesis of 1-trimethylsilyl-3,6,6-trimethyl-3-ethyl-1,4-heptadiyne (5). To a Grignard reagent (prepared from 2.4 g of Mg and 10.9 g of C_2H_5Br) was added, over a period of 25 min and with continuous stirring and cooling, 8.5 g of tert-butylacetylene in 20 ml of ether. The contents of the flask were allowed to stand for 40 hr, and were then heated on a water bath to 35° and held at this temperature until there was no further evolution of ethane. To the resulting complex – tert-butylacetylenemagnesium bromide – was added 1 g of Cu_2Cl_2 and 0.5 g of $HgCl_2$ as a catalyst [3]. The mixture was stirred for 0.5 hr and then cooled to −2°, and 21.68 g of the acetylenic chloride [2] was added to it. The contents of the flask were maintained at room temperature for 58 hr, with stirring, after which they were heated for 6 hr and decomposed with dilute HCl. The ether solution and extract were dried over calcined

	Compound	B. p., °C (mm Hg)	d_4^{20}	n_D^{20}	MR_D		Yield, %	C. %		H. %		Si. %		Cl. %	
					calc.	found		calc.	found	calc.	found	calc.	found	calc.	found
1	$(CH_3)_2ClC-C\equiv C-Si(CH_3)_3$	32—35 (5)	0,9043	1,4503	52,03	51,95	55,4	54,96	54,81 54,71	8,65	8,67 8,70	16,07	15,41 15,60	20,31	20,47 20,10
2	$CH_3C_2H_5Cl-C-C\equiv CSi(CH_3)_3$	38—40 (2)	0,9015	1,4502	56,66	56,30	63,8	57,24	57,49 57,45	9,07	9,22 9,15	14,87	14,50 14,20	18,80	18,84 18,71
3	$(CH_3)_3C-C(CH_3)Cl-C\equiv CSi(CH_3)_3$	54—55 (2) m. p. 41	—	—	—	—	63,0	60,91	61,10 61,20	9,76	9,87 9,98	12,96	12,51 12,40	16,36	15,40 15,60
4	$(CH_3)_3C-C\equiv C-C(CH_3)_2-C\equiv C-Si(CH_3)_3$	53—54 (4)	0,8245	1,4526	73,36	72,21	50,0	76,28	76,00 76,10	10,97	11,20 11,10	12,74	12,35 12,20	—	—
5	$(CH_3)_3C-C\equiv C-C(CH_3)(C_2H_5)-C\equiv C-Si(CH_3)_3$	56—58 (2)	0,8035	1,4368	77,99	76,39	59,7	76,84	77,18 77,06	11,17	11,29 11,36	11,98	11,65 11,78	—	—
6	$(CH_3)_3C-C\equiv C-C(CH_3)[C(CH_3)_3]-C\equiv CSi(CH_3)_3$	70—72 (4) m.p. 55	—	—	—	—	45,5	77,77	77,84 77,80	11,51	11,70 11,76	10,70	10,11 10,25	—	—

Na_2SO_4. After distillation of the ether, two distillations yielded 14 g (59.7%) of 1-trimethylsilyl-3,6,6-trimethyl-3-ethyl-1,4-heptadiyne with a b. p. of 56-58° (2 mm). Two additional representatives of diacetylenic silicohydrocarbonds were prepared by a similar route. The constants of these compounds are shown in the table.

Hydrogenation of the Diacetylenic Silicohydrocarbon [5].*

A total of 0.2 g of Raney Ni catalyst in 5 ml of methyl alcohol was used. The mixture was saturated with hydrogen, after which 0.123 g of the silicohydrocarbon [5] was introduced.

The addition of hydrogen proceeded vigorously for the first 13 min, and 11 ml was absorbed. The absorption of hydrogen then took place slowly, and an additional 34.61 ml of hydrogen was absorbed. A total of 11 + 34.61 + + 43.61 ml of hydrogen was absorbed. Theoretically, 47 ml of hydrogen is required for hydrogenation of two triple bonds.

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* Hydrogenation of the diacetylenic silicohydrocarbon was carried out in the laboratory of Prof. L. Kh. Freidlin with the help of I. F. Zhukova, to whom we express our appreciation.

ANIONIC POLYMERIZATION IN THE PRESENCE OF AROMATIC COMPOUNDS

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The generally accepted mechanism of polymerization in the presence of metal arene initiators [1, 2] assumes participation of the aromatic component only in the initiation step (transfer of an electron from the aromatic radical ion to the monomer). The possibility of the participation of aromatic hydrocarbons in anionic chain growth has not been considered up to the present.

We have established that anthracene causes a sharp decrease in the rate of anionic polymerization of styrene initiated by sodium arene complexes in tetrahydrofuran, and the magnitude of the decrease depends essentially on the ratio of anthracene to styrene. If the rate constant for chain growth, or anionic polymerization of styrene in THF at 25° is 285-570 liters/mole·second [3], in the presence of anthracene the observed rate constant (polymerization rate divided by the concentration of active centers and monomer) at 20° is of the order of 0.1 liters/mole/second at a molar ratio of anthracene to styrene of 1:30 and $3 \cdot 10^{-3}$ liters/mole·second at a ratio of anthracene to styrene of 1:6.

The inhibiting effect of anthracene is observed both when it is introduced together with the initiator (sodium naphthalene or sodium anthracene) and when it is added as a styrene–anthracene mixture to the "living" polystyrene prepared with sodium naphthalene or biphenylsodium initiator. The polymerization rate is constant up to a conversion of 30-40%. The molecular weight of the polymers, except for that prepared with sodium anthracene initiator in the absence of free anthracene, agrees with the molecular weight calculated by the following formula to within 10%:

$$\overline{M} = \frac{2M_0}{K}, \qquad (I)$$

where M_0 is the amount of monomer in grams and K is the amount of initiator in moles.

The above facts indicate that the process proceeds with a constant number of active centers (equal to the amount of initiator charged) and with no chain transfer. Consequently, the retardation is not connected with a decrease in the number of active centers as a consequence of a shift of the following equilibrium to the left:

$$A^{\cdot} + C \rightleftarrows A + C^{\cdot} \qquad (II)$$

(A and S represent, respectively, anthracene and styrene; the asterisk indicates a radical ion, i.e., a molecule having an excess electron). Complete transfer of the excess electrons from anthracene to styrene is accomplished. The absence of $A^{\cdot}$ from the system was also confirmed spectrophotometrically. This fact may seem strange, since the equilibrium constant for reaction (II) at 25° is 10^{-7} (a difference of standard potentials of −0.41 v [4]), and even at an anthracene–styrene ratio of 1:10, the equilibrium concentration of $C^{\cdot}$ radical ions is less than the concentration of $A^{\cdot}$ by a factor of 10^6. Apparently the complete disappearance of $A^{\cdot}$ is brought about by the irreversible consumption of $C^{\cdot}$ as a consequence of reaction with the monomer and recombination [2], and the very low consumption of monomer in the initial stage is a consequence of the sharp decrease in the rate of chain growth in the presence of anthracene. When the polymerization is carried out with sodium anthracene in the absence of free anthracene, there is an increase in the molecular weight by a factor of 1.5-2 as compared to that calculated by Eq. (I): however, in this case, in spite of the high reaction rate, $A^{\cdot}$ ions are not observable spectroscopically after completion of polymerization.

Thus, the rate- decreasing effect is associated with the participation of anthracene in chain growth reactions. In all probability, copolymerization of anthracene and styrene takes place. It is known that anthracene is very active in radical reactions [5]; radical copolymerization of anthracene with butadiene has been described [6]. To the present time, there have been no reports of the participation of anthracene in anionic copolymerization. It might be expected that by adding to the styrene carbanion, it would form a rather stable anion which would have low activity owing to significant delocalization of the charge. The observed kinetic effects are in good agreement with such concepts.

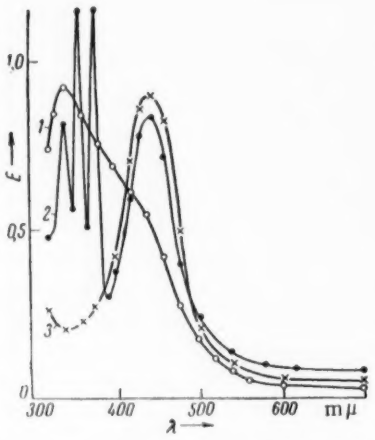

Fig. 1. Electronic absorption spectra of the anthracene–polystyrene system in THF.

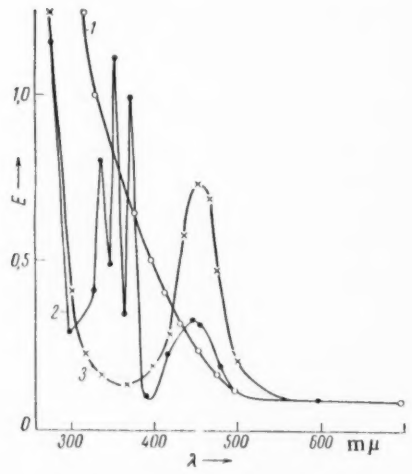

Fig. 2. Electronic absorption spectra of the system polybutadiene–anthracene in THF. 1) Living polymer prepared with sodium naphthalene; 2) same with the addition of anthracene; 3) same after polymerization of a new portion of monomer.

We carried out the following experiment in order to confirm the assumption that copolymerization of anthracene with styrene takes place. Anthracene in an amount twice that of the active centers was added to a solution of "living" polystyrene prepared with sodium naphthalene. In the electronic absorption spectrum of the system, taken after addition of the anthracene, peaks due to free anthracene (341, 358, and 378 mμ) are clearly visible; at the same time, there is a shift of the absorption maximum of the "living" polymer from 340 mμ to 445 mμ (see Fig. 1, curves 1 and 2). Practically no free anthracene was observed (curve 3) in the system after polymerization of additional amounts of styrene, which confirms its participation in copolymerization with styrene.

Curve 3 clearly shows that the shifted position of the absorption maximum in the spectrum of the "living" polymer remains after polymerization of new portions of monomer. The polymer prepared with sodium anthracene also has an absorption maximum at 445 mμ. Similar phenomena have recently been observed by Levy and co-workers [7]. In contrast to the spectrum of ordinary "living" polymer, which is substantially changed a day after preparation of the polymer [8], the spectrum of the polymer prepared in the presence of anthracene exhibited practically no change over a period of three days. As in [7], the observed shift in the spectra can be explained by complex formation between the anthracene and active polymerization centers. It is possible, however, that the shifted maximum at 445 mμ corresponds to the anthracene carbanion, which is present at the ends of the polymer chains. This assumption is also in agreement with the experimental data if the anthracene carbanion has an extinction coefficient at 445 mμ which is substantially greater than that of the styrene carbanion at 340 mμ.

We note that shifting of the maximum in the spectrum of polymer prepared with sodium anthracene, whatever may be the nature of this phenomenon, indicates that here there is scarcely any initiation with the addition of the aromatic component to the monomer, as has been postulated in some cases [2, 9]. If this were the initiation mechanism, as a consequence of the absence of free anthracene from the system the polymer would have the usual spectrum. Moreover, in the light of the above data it is clear that observations of initiator fragments in polymers, as described in [2, 9], cannot themselves serve as proof of the occurrence of initiation by such means, since aromatic components could enter the chain during chain growth.

The presence of significant amounts of naphthalene (up to 50% with respect to the styrene) does not have an appreciable effect on the rate of the process or on the molecular weight, but it does substantially change the spectrum of the "living" polymer – the maximum at 340 mμ disappears, and maxima appear at 430 and 550 mμ.

The polymer retains the ability to add new portions of monomer, but the changed spectrum remains upon further addition of monomer. Similar changes in the spectrum of "living" polystyrene on standing have been noted [8, 10]; it is possible that in this case slow interaction with the aromatic component of the initiator took place.

It may be expected that the inhibiting effect of anthracene on the polymerization of less active monomer will be still greater, both as a consequence of the lower activity of the monomer and as a consequence of the greater rate of addition of anthracene to the active centers. In agreement with this, it has been shown that polymerization of butadiene at 20°, which is less active than styrene in anionic polymerization [11], is practically stopped at an anthracene – butadiene ratio of 1:30. As in the case of styrene, the addition of anthracene to "living" polybutadiene causes a change in the spectrum, with the appearance of a maximum at 450-460 mμ (see Fig. 2, curves 1 and 2). Polymer prepared with sodium anthracene exhibits the same changed spectrum. This spectrum, with a maximum at 450-460 mμ, is retained after polymerization of new portions of monomer (curve 3, the free anthracene disappears during the additional polymerization). The spectrum remains practically unchanged over a period of five days. "Living" polybutadiene apparently interacts with anthracene in the same manner as "living" polystyrene.

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THE SOLUBILITY OF NITROGEN IN LIQUID MANGANESE

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The solubility of nitrogen in liquid manganese has previously been studied [1-4]. However, the results of the investigations of the various investigators are contradictory. Thus, the solubility of nitrogen in liquid manganese at 1300-1400 (1450) °C has been reported as 0.10-0.13% [1], 3.7% [2], 1.0% [3], and 1.58-1.95% [4]. The use of the "hot volume" method for determining the solubility of nitrogen in liquid manganese is undesirable owing to the high vapor pressure of liquid manganese. The interaction of the condensate with gaseous nitrogen, which results in the formation of Mn_4N, leads to substantial error.

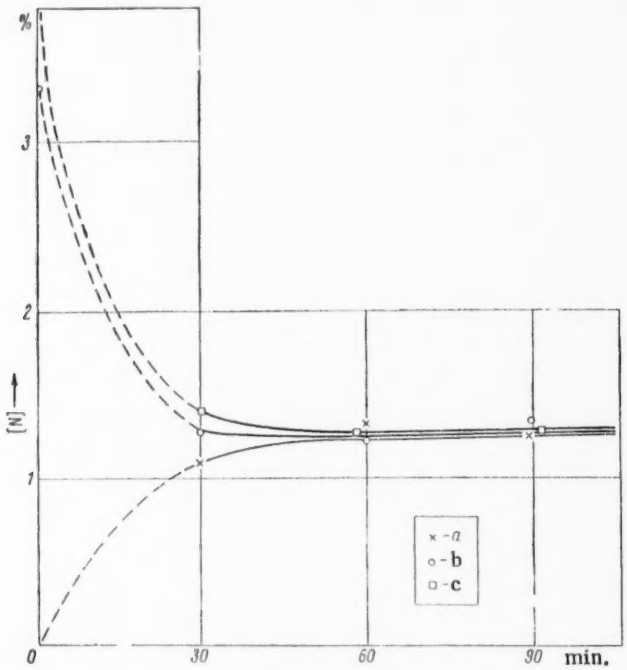

Fig. 1. Kinetic curves for: nitriding of liquid Mn (a), denitriding of liquid Mn containing 3.3% N (b), denitriding of liquid Mn containing 6.0% N (c).

We chose rather to investigate the dynamic equilibrium between liquid manganese and a gas phase consisting of nigrogen or a mixture of nitrogen and hydrogen. The partial pressure of nitrogen in the gas phase at the instant equilibrium is attained determines the activity of the nitrogen in the metal. The equilibrium nitrogen content of a sample of the solid, rapidly cooled metal was then determined. The method and apparatus for the study of the solubility of nitrogen in metal melts has been described previously [5].

Manganese	Content, %					
	C	Fe	Si	S	P	N
Remelted electrolytic	0,06—0,08	0,05—0,06	0,04	0,05—0,06	0,003	—
Nitrided electrolytic	0,06—0,08	0,05—0,06	0,05	0,05—0,06	0,003	3,3 and 6,0

An LG-60 high frequency vacuum tube oscillator was used to heat the metal. Electrolytic manganese, which had undergone a preliminary remelting, and nitrided electrolytic manganese were used as the starting materials. The contents of various elements in the manganese are shown in the table.

In series I, the metal was maintained for a period of 120-180 min at the desired temperature and under the desired nitrogen and hydrogen flow (40 and 1100 ml/min, respectively), and samples of the metal were collected. The sample solidified almost immediately (less than 1 second). In series II, the melt was maintained under the same conditions, and samples were collected at 30, 60, 90, and 120 min.

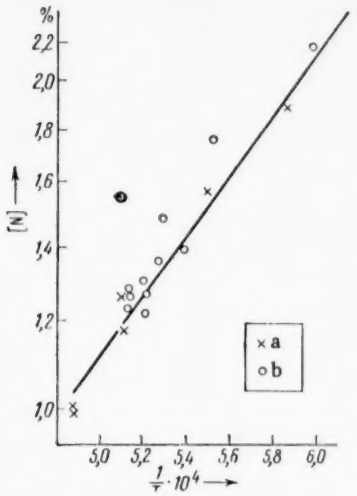

Fig. 2. The effect of temperature on the solubility of N in liquid Mn. a) Mn; b) nitrided Mn.

With the aim of freeing the manganese from oxygen, in both series the liquid melt was held for 60 min in a stream of purified hydrogen (400 ml/min), and the flow was then discontinued. The solidified metal was again remelted and held at the desired temperature and under the desired hydrogen and nitrogen flow (40 and 1100 ml/min, respectively). In a third series, the molten manganese, which contained 3.3 and 6.0% N, was held under the same conditions for 60-120 min without preliminary purification in hydrogen.

The nitrogen content of the manganese was determined chemically [6].

As remarked above, at a given temperature equilibrium was reached both by saturating the liquid manganese with nitrogen and by removal of nitrogen from the nitrided manganese. It was found (Fig. 1) that holding the metal in the gas flow for one hour was quite sufficient for the establishment of equilibrium.

The solubility of nitrogen in liquid manganese decreased with an increase in temperature (Fig. 2). This relationship can be represented by the following equation:

$$1/2\,N_2\,(g) \rightleftarrows [\%\,N],\ K = \frac{a_N}{P_{N_2}^{1/2}} = \frac{f_N\,[\%N]}{P_{N_2}^{1/2}}. \qquad (1)$$

Molten manganese in equilibrium with nitrogen at a pressure of 1 atm was taken as the standard state. On the basis of the experimental data, at $P_{N_2} = 1$ atm and $f_N = 1$.

$$\lg K = \lg [\%\,N] = \frac{3010}{T} - 1{,}457; \qquad (2)$$

$$\Delta F^0 = -13780 + 6{,}65\,T. \qquad (3)$$

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A NEW METHOD FOR THE SYNTHESIS OF LARGE-RING CYCLIC KETONES WITH THE ODOR OF MUSK

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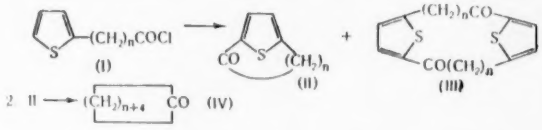
Through the synthesis of cyclotetradecanone [1], we have previously shown that higher alicyclic ketones can be prepared by reductive desulfurization of the products of intramolecular acylation of the chlorides of ω-thienylalkanecarboxylic acids* (I):



Cyclization of the acid chlorides was carried out in carbon disulfide using a finely dispersed condensation agent formed by the addition of an ether solution of technical aluminum chloride to carbon disulfide. It was later found that carbon disulfide can successfully be replaced by chloroform [2].

Special comparison experiments showed that the total yield of cyclization products and the ratio of the yields of these products depend essentially on the phase composition of the reaction mixture. When intramolecular acylation of 10-thienylcapryl chloride was carried out in a homogeneous medium (aluminum chloride etherate purified by distillation was used), the yield of (10)-α-cyclothien-1-one** (II, n = 9) decreased from 40 to 20%, and the yield of (10, 10)-α-cyclodithien-1,15-dione (III, n = 9) decreased from 30 to approximately 10% with a simultaneous increase in the amount of tar formed. Thus, the yield of cyclization products was two to three times less than when the reaction was carried out in a heterogeneous medium under the conditions previously described [1, 2].

A study of the nature of the condensation agent led us to think that its heterogeneity was due to the presence in the technical aluminum chloride of hydrolysis products due to atmospheric moisture. Assuming that heterogeneity of the condensation agent should promote the intramolecular cyclization process by adsorbing the molecules undergoing cyclization and thereby limiting their mobility, we designed a series of experiments with the product of the partial hydrolysis of aluminum chloride etherate (1 mole of water per mole of etherate), which forms a very fine suspension in chloroform. It was found that this increased the yield of α-cyclothien-1-one (II) by a factor of approximately 1.5 with a simultaneous decrease in the amount of the other cyclization product – diketone III. This condensation agent was used to carry out condensation of the chlorides of 10-thienylcapric, 11-thienylundecanoic, 12-thienyllauric, and 13-thienyltridecanoic acids. The condensations gave yields of 53-63% of monoketones of type II with n = 9, 10, 11, and 12, reductive desulfurization of which gave 75-90% yields of the alicyclic ketones, which had the odor of musk – cyclotetradecanone, cyclopentadecanone (exaltone), cyclohexadecanone, and cycloheptadecanone (dihydrocivetone). The overall yield of alicyclic ketones calculated on the ω-thienylalkanecarboxylic acids was 40-55%, depending on the size of the ring.

Owing both to its simplicity and to the yields (cf., for example, the recently described syntheses of exaltone [3, 4] and dihydrocivetone [3, 5]), the method proposed here should be useful for preparative purposes.

EXPERIMENTAL

Technical aluminum chloride was used for the preparation of the aluminum chloride etherate. The etherate was purified by vacuum distillation; b. p. 100-103°/0.5 mm, 108-110°/1 mm, 124-125°/3mm, 128-129°/4 mm, and about 150°/12 mm (with decomposition); m. p. about 35°. Yields of up to 85% were obtained. The following are

reported in the literature: b. p. 108°/2-3 mm [6] and 147°/11 mm [7]; m. p. 33-36° [6-8]. The distilled product was completely soluble in chloroform and carbon disulfide, forming transparent solutions which underwent no change on boiling without access to moisture.

The ω-thienylalkanecarbonyl chlorides were prepared by the action of thionyl chloride on the ω-thienylalkanecarboxylic acids (the latter were prepared by the method of [9]) in absolute ether (cf. [1]). The melting points and yields of these acid chlorides, which were subsequently subjected to cyclization, are presented in the table.

TABLE 1. ω-Thienylalkanecarbonyl Chlorides (I)

	n = 9	n = 10	n = 11	n = 12
B. p., °C/mm	157 – 160/1	154 – 155/0.2	175 – 180/0.7	Decomposed during an attempt to distill at 0.2 mm
Yield, %	92	91	76	

TABLE 2. α-Cyclothien-1-ones (II)

n	B. p., °C/mm	M. p., °C	Yield, %	M. p. of semicarbazone, °C
9	149—152/1,0	40—41 [1]	53,6 [2]	188,5—189,5 [3]
10	128—132/0,05	44,5—46,5 [4]	63,5	194—196 [4]
11 [5]	162—165/0,5	31—32	62,5 [2]	214—215
12 [6]	157/0,005	—	60,0	225—226,5

[1] Prepared by vacuum distillation with subsequent pressing on a porous plate; the (10)-α-cyclothien-1-one described by us previously [1] melted at 35-35.5°

[2] Yields of the order of 40% [1, 2] were obtained when the previously described catalyst [1] was used.

[3] Found %: N 14.29, 14.41. $C_{15}H_{23}N_3OS$. Calculated %: N 14.32.

[4] A mixture with a sample prepared earlier [10] showed no depression of the melting point.

[5] Found %: C 72.64, 72.42; H 9.17, 9.28; S 12.09, 12.12. $C_{16}H_{24}OS$. Calculated %: C 72.66; H 9.14; S 12.13.
Semicarbazone: Found %: N 13.13, 12.89. $C_{17}H_{27}N_3OS$. Calculated %: N 13.07.

[6] $n^{20}D$ 1.5448, d^{20}_4 1.0480; MR_D found 83.98, calculated 83.79. Found %: C 73.20, 73.12; H 9.16, 9.36; S 11.20, 11.31. $C_{17}H_{26}OS$. Calculated %: 73.31; H 9.41; S 11.52.
Semicarbazone: Found %: N 12.28, 12.23. $C_{18}H_{29}N_3OS$. Calculated %: N 12.53.
In contrast to the preceding cases, the yield of (13)-α-cyclothien-1-one is based not on the acid chloride, but on the 13-thienyltridecanoic acid, the chloride of which was used without purification.

Intramolecular acylation of the ω-thienylalkanecarbonyl chlorides was carried out in an apparatus consisting of a 3-liter flask with a thermometer, a stirrer, and a special head for working under extreme-dilution conditions; the head was fitted with a reflux condenser and a syringe for uniformly introducing the solution of acid chloride [1]. A solution of approximately 0.3 mole of aluminum chloride etherate in 300 ml of absolute ether was placed in the flask, and an equimolar amount of water was charged to the high-dilution head. When the ether was boiled, water gradually dissolved in the ether and fell with the stream of condensate into the etherate solution.* When the water had dissolved (after apprimately 10 hr), 1.5 liters of dry chloroform was added to the flask, the head and reflux condenser were replaced by 2 column with a total condenser, and the ether was distilled off until the temperature in the top of the column reached 60-61°. This caused the formation of a fine suspension of the catalyst. The high-dilution head with reflux condenser and syringe was then substituted for the column, the chloroform was brought to boiling,

* By replacing the head with an extractor for use with a high-boiling solvent, hydrolysis of the etherate can be carried out in chloroform.

and a solution of 0.015-0.03 mole of the ω-thienylalkanecarbonyl chloride was added to the flask at a rate of $7 \cdot 10^{-4}$ – $8 \cdot 10^{-4}$ mole per hour. After the usual treatment of the resulting mixture, the respective α-cyclothien-1-ones were separated by crystallization, distillation, or high-vacuum distillation. The constants and yields of the cyclization products are presented in Table 2.

Reductive desulfurization of the α-cyclothien-1-ones. A solution of 1 g of the α-cyclothien-1-one in 70 ml of alcohol containing 15-20% acetone was stirred at 25-35° with a 3-5 fold amount (by weight) of skeletal nickel until a negative test for sulfur was obtained (about 2 hr). After separation of the skeletal nickel and elimination of the solvent, the respective large-ring alicyclic ketone was obtained.

The yield of cyclotetradecanone from (10)-α-cyclothien-1-one (II, n = 9) was 85% (cf. [1]), and the yield of exaltone from (11)-α-cyclothien-1-one (II, n = 10) was 75% (cf. [10]).

Reductive desulfurization of (12)-α-cyclothien-1-one, (II, n = 11) gave an 86% yield of cyclohexadecanone (IV, n = 11), m. p. 62.5-64°.

Found %: C 80.04, 80.19; H 12.39, 12.30. $C_{16}H_{30}O$. Calculated %: C 80.60; H 12.68.

The semicarbazone melted at 178-180.5°.

Found %: N 14.27, 14.49. $C_{17}H_{33}N_3O$. Calculated %: N 14.22.

Literature data for cyclohexadecanone: m. p. 63-64° [11], 65° [12]. semicarbazone, m. p. 180-181° [11], 179° [12].

Hydrogenolysis of (13)-α-cyclothien-1-one (II, n = 12) gave a 90% yield of dihydrocivetone (IV, n = 12), m. p. 61-63°.

Found %: C 80.75, 80.83; H 12.56, 12.50. $C_{17}H_{32}O$. Calculated %: C 80.88; H 12.78.

The semicarbazone melted at 189.5-191°.

Found %: N 13.87, 13.71. $C_{18}H_{35}N_3O$. Calculated %: N 13.58.

Literature data for dihydrocivetone, m. p. 63° [13], 64° [5]; semicarbazone, m. p. 191-191.5° [5], 191° [13].

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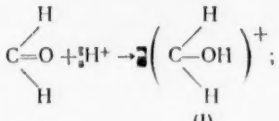
HYDROXYMETHYLATION OF PHOSPHINE AND ITS DERIVATIVES

E. I. Grinshtein, A. B. Bruker, and L. Z. Soborovskii

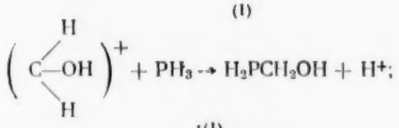
(Presented by Academician I. L. Knunyants, March 16, 1961)
Translated from Doklady Akademii Nauk SSSR, Vol. 139, No. 6, pp. 1359-1362, August, 1961
Original article submitted March 15, 1961

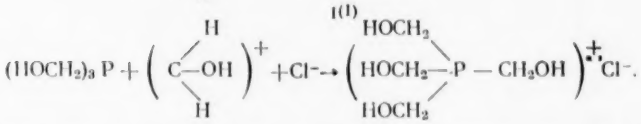
It has been known for some time that phosphine as well as alkyl- and arylphosphines are capable of reacting with formaldehyde only when hydrochloric acid or certain salts take part in the reaction. The products of these reactions are phosphonium compounds, for example, tetra(hydromethyl)phosphonium chloride, which is obtained as a result of the reaction of phosphine with an aqueous solution of formaldehyde and hydrochloric acid [1-5].

According to the mechanism which has previously been proposed for this reaction[6], the reaction proceeds through the intermediate formation of formaldehyde cation (I), which then reacts with a molecule of phosphine with elimination of a proton and which is thereby converted initially into the monohydroxymethyl derivative (II) and then to di- and tri(hydroxymethyl)phosphines and finally to tetra(hydroxymethyl)phosphonium chloride:

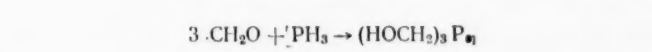


(I)

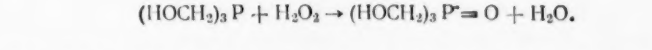




We have found that the reaction of formaldehyde with phosphine can take place by another mechanism with the formation of the corresponding derivatives of trivalent phosphorus. Thus, paraformaldehyde interacts with phosphine (at a molar ratio of 3:1 at 80-100° forming, in good yield, tri(hydroxymethyl)phosphine according to the equation:



Oxidation of the resulting tri(hydroxymethyl)phosphine with a dilute solution of hydrogen peroxide gave tri-(hydroxymethyl)phosphine oxide:



Our experiments showed that methylphosphine reacts more readily with paraformaldehyde than does phosphine (at a lower temperature and shorted contact time) giving di(hydroxymethyl)methylphosphine a liquid boiling at 90° 3 mm; this compound has not previously been described.

The di(hydroxymethyl)methylphosphine was oxidized with hydrogen peroxide with the formation of the previously unknown oxide:

$$(HOCH_2)_2PCH_3 + H_2O_2 \rightarrow (HOCH_2)_2P(=O)CH_3.$$

Dimethylphosphine reacts still more easily with paraformaldehyde forming dimethyl(hydroxymethyl)phosphine:

$$(CH_3)_2PH + CH_2O \rightarrow (CH_3)_2PCH_2OH.$$

It should be remarked that the latter compound belongs to a previously undescribed type of monohydric alcohols containing an organophosphorus radical joined to the hydroxylated carbon atom.

The fact that in our experiments phosphine and the organic phosphine derivatives react with formaldehyde under conditions such that there is no source of protons, which are required for the formation of formaldehyde cations, provides a basis on which to assume that the reaction proceeds through an electrophilic attack by the carbonyl carbon atom on the phosphorus atom of the phosphine molecule, which leads to the formation of a hydroxymethylphosphine.

The latter compound is further converted to the corresponding di- and trihydroxymethyl derivative. This assumption is in good agreement with our observation, noted above, that methyl- and dimethylphosphine more easily react with paraformaldehyde than does phosphine itself. This is due to strengthening of the electron-donor properties of phosphorus, which increases in the series:

$$PH_3 < CH_3 - PH_2 < (CH_3)_2PH\ (^7).$$

Through the use of this method it is possible to prepare different hydroxyalkyl-substituted phosphines merely by using all of the possible alkyl- and arylphosphines and carbonyl compounds.

EXPERIMENTAL

1. Preparation of di(hydroxymethyl)methylphosphine. To 150 cm^{-3} stainless steel cylindrical reaction vessel fitted with a pressure gauge and a valve was charged 17.7 g of paraformaldehyde* (calculated 100% CH_2O: 16.8 g, 0.56 mole) and 10.1 g of methylphosphine (0.21 mole). After the introduction of the components, the reaction vessel was heated to 82-85° and shaken for 40 min. The maximum pressure in the cylinder was 6 atm, gauge, at 73°, but the pressure had decreased to 0 atm, gauge, after 3 min. There was obtained 26.9 g of reaction products in the form of a sirupy liquid having an odor like that of phosphines.

Pure di(hydroxymethyl)methylphosphine with a b. p. of 89-90°/3 mm was separated by distillation of the reaction product under vacuum (the major portion of the product distilled at 90°). The yield was 18.9 g or 83% of theoretical, calculated on the methylphosphine. The di(hydroxymethyl)methylphosphine was a viscous, transparent liquid which did not crystallize on cooling; $n^{20}D$ 1.5325, d^{20}_4 1.157; MR found 28.95, calculated 29.34.

Found %: C 33.48; H 8.59; P 28.43. $C_3H_9O_2P$. Calculated %: C 33.34; H 8.34; P 28.70.

The substance was readily soluble in water and alcohol and difficultly soluble in nonpolar solvents. The aqueous solution had a basic reaction.

2. Preparation of di(hydroxymethyl)methylphosphine oxide. To 26.4 ml of a 6% aqueous solution of hydrogen peroxide (cooled with ice) was gradually added, with continuous stirring, a solution of 4.9 g of "crude" di(hydroxymethyl)methylphosphine [containing about 81% $CH_3P(CH_2OH)_2$] in 10 ml of water. The aqueous solution obtained at the conclusion of the reaction was filtered and evaporated under vacuum to constant weight. There was obtained 4.65 g (98.5%) of di(hydroxymethyl)methylphosphine oxide in the form of a very viscous, sirupy liquid. Complete crystallization of the liquid was induced by cooling and scratching, and colorless acicular crystals which deliquesced in air were obtained.

This substance did not distill when heated to 200° under reduced pressure, nor did it decompose. The product was soluble in water and alcohol and insoluble in nonpolar solvents (benzene, ether).

* In this and other phosphine reactions described in the present paper, paraformaldehyde containing 95% formaldehyde (polymeric form) was used.

Found %: C 29.24; H 7.25; P 24.10. $C_3H_9O_3P$. Calculated %: C 29.03; H 7.26; P 25.00.

3. Preparation of hydroxymethyldimethylphosphine. To the same reaction vessel used in Expt. 1 was charged 4.84 g of paraformaldehyde (calculated 100% CH_2O: 4.6 g or 0.153 mole) and, after evacuation 10.1 g (0.163 mole) of dimethylphosphine. The cylinder containing the reaction mixture was heated and shaken for 1 hr at 65-67°. There was obtained 14.2 g of reaction product. This was distilled under vacuum, and a fraction boiling at 50-51°/10 mm was collected. This fraction was pure hydroxymethyldimethylphosphine. The yield was 12.1 g or 80.7% of theoretical (calculated on the dimethylphosphine). The transparent, mobile liquid boiled at 70°/30 mm; $n^{20}D$ 1.5011, d^{20}_4 0.9931. MR found 27.29, calculated 27.83.

Found %: C 39.17; H 9.78; P 34.1. C_3H_9OP. Calculated %: C 39.13; H 9.89; P 33.7.

4. Preparation of tri(hydroxymethyl)phosphine. The reaction was carried out in the same reaction vessel used in Expts. 1 and 3. The charge consisted of 26.0 g of paraformaldehyde (calculated 100% CH_2O: 0.821 mole) and 9.77 g (0.286 mole) of phosphine. The cylinder was heated (and shaken) at 100° for about 2 hr. The highest pressure reached was 35-40 atm, and it gradually dropped as the phosphine reacted. Upon completion of the reaction, the unreacted phosphine (0.26 g) was separated. There was obtained 34.25 g of crude reaction product in the form of a light colored, sirupy liquid with a characteristic phosphine odor. It gradually crystallized to almost colorless hygroscopic needles with an m. p. of 51-53°.

The yield was about 94%, calculated on the phosphine reacted.

Found %: C 29.26; H 7.57; P 24.2. $C_3H_9O_3P$. Calculated %: C 29.0; H 7.26; P 25.0.

The substance distilled under reduced pressure with appreciable decomposition (b. p. 111-113°/2.5 mm). It was readily soluble in water and alcohol and insoluble in nonpolar organic solvents. The aqueous solution was neutral. The product gradually decomposed during storage (an orange color and acid impurities appeared).

5. Preparation of tri(hydroxymethyl)phosphine oxide. To 27 ml of a 7% aqueous solution of hydrogen peroxide (0.054 mole of H_2O_2), which was cooled with ice, was gradually added,* with continuous stirring, 6.45 g (0.053 mole) of tri(hydroxymethyl)phosphine. The aqueous solution obtained upon completion of the reaction was filtered and evaporated under vacuum to constant weight. There was obtained 6.92 g (95.0% yield) of tri(hydroxymethyl)phosphine oxide in the form of a transparent, colorless, viscous sirup. Upon cooling, this completely crystallized to colorless, very hygroscopic crystals, which, after recrystallization from ethyl alcohol, melted at 56-58°. The substance was insoluble in benzene and ether. The product did not contain trivalent phosphorus, and, in contrast to tri(hydroxymethyl)-phosphine, it did not decompose during storage.

Found %: C 25.88; H 6.28; P 21.60. $C_3H_9O_4P$. Calculated %: C 25.71; H 6.43; P 22.15.

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* It is also possible to pour an aqueous or alcoholic solution of tri(hydroxymethyl)phosphine into the calculated amount of hydrogen peroxide solution, or vice versa.

NEW SYNTHESES OF C-SUBSTITUTED CARBOHYDRATES

Yu. A. Zhdanov and G. A. Korol'chenko

(Presented by Academician A. I. Oparin, March 16, 1961)
Translated from Doklady Akademii Nauk SSSR, Vol. 139, No. 6, pp. 1363-1366, August, 1961
Original article submitted March 16, 1961

It is possible to prepare C-substituted carbohydrates with relatively simple radicals (phenyl, tolyl, anisyl, etc.) by ordinary organomagnesium synthesis. A large number of such carbohydrate derivatives with more complex radicals have been prepared by further treatment of the products obtained by Grignard synthesis. Thus, glycopyranosylarylamines have been prepared by successive nitration and reduction of the corresponding glycopyranosyl derivatives [1, 2].

We have undertaken to extend the scope of the radicals which may be introduced into carbonhydrates via Grignard synthesis. The direct introduction of an aglycon containing an amino group into the sugar seemed to be of interest. Amines with protected (for example, methylated) amino groups are suitable for this purpose, since a free amino group reacts with the Grignard reagent. Aryl bromides containing an amino group para to the halogen react with magnesium only in the presence of a catalyst. Therefore, we prepared dimethylaminophenylmagnesium bromide by the action of a mixture of equivalent amounts of p-bromodimethylaniline and ethyl bromide on magnesium. This product reacted with acetochloroglucose to give p-glucopyranosyldimethylaniline in a yield of 25.4% of theoretical; the compound was isolated as the tetraacetate.

An attempt to combine glucose with dimethylaniline through dimethylaminophenyllithium was less successful. The reaction of lithiodimethylaniline gave only a 1.6% yield of the end product. The use of organolithium compounds for the synthesis of C-substituted carbohydrates has failed to give good results in other cases also. In the reaction of phenyllithium with acetochloroglucose, the yield of phenylglucose amounted to only 9.4% of theoretical [3], and the interaction of picolyllithium with acetobromoglucose has not generally led to the formation of C-substituted derivatives of glucose [4].

We prepared glucopyranosyldimethylhydroquinone from acetochloroglucose and dimethylhydroquinonylmagnesium bromide. The low yield of product (18.8%) may be explained by the low solubility of the original bromide in ether and also by steric hindrance. The synthesis of p-allylglucopyranosylbenzene did not present any special difficulties. In addition to previously described rhamnose derivatives [5], we were able to prepare the acetates of rhamnopyranosylthiophene (obtained as a sirupy liquid) and crystalline rhamnopyranosylanisole by the interaction of acetochlororhamnose with α-iodothiophene and p-bromoanisole, respectively. The thamnopyranosylanisole was also obtained in the free state.

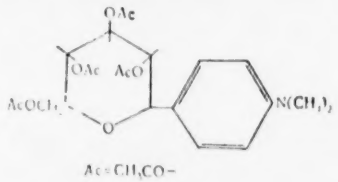
EXPERIMENTAL

p-Tetraacetyl-D-glucopyranosyldimethylaniline. A solution of p-dimethylaminophenylmagnesium bromide was prepared by the interaction of 7.86 g (0.32 mole) of magnesium with a solution of 32.75 g (0.16 mole) of p-bromodimethylaniline and 17.44 g (0.16 mole) of ethyl bromide in 100 ml of absolute ether. To this solution was added a solution of 5 g (0.013 mole) of acetochloroglucose in 75 ml of absolute ether. The reaction mixture was stirred for 2 hr at room temperature and then for an additional 5 hr on a hot water bath. When the reaction was complete, 50 ml of water was added to the mixture as it was cooling, and the aqueous layer was separated and evaporated to dryness. The dry residue was acetylated with acetic anhydride in the presence of sodium acetate. The acetylated product was extracted with ether, and the ether extract was decolorized with carbon and dried over calcium chloride.

The ether was evaporated, and the resulting thick, viscous mass was recrystallized from isopropyl alcohol and then from ethyl alcohol. The crystalline product amounted to 1.6 g (25.4% of theoretical). The lustrous white needles melted at 169-170°; they were soluble in ether, chloroform, methyl alcohol, and hot ethyl and isopropyl alcohols, and were insoluble in water and petroleum ether. This is the first description of the product.

Found %: C 58.48; H 6.54; N 3.23. $C_{22}H_{29}P_9N$. Calculated %: C 58.53; H 6.43; N 3.10.

The structure of the substance is represented by the formula:



p-D-glucopyranosyldimethylaniline. A solution of 1.3 g of tetraacetyl-D-glucopyranosyldimethylaniline in 100 ml of absolute methyl alcohol was saturated with dry ammonia and allowed to stand overnight. The methyl alcohol was evaporated, and the resulting sirup was washed with ether and recrystallized from methyl acetate.

There was obtained 0.65 g (79.7% of theoretical) of a white crystalline substance with an, m. p. of 88-90°. It was soluble in water, lower alcohols and methyl acetate and insoluble in ether. It is described here for the first time.

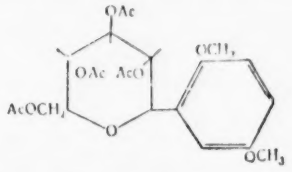
Found %: N 5.18. $C_{14}H_{21}O_5N$. Calculated %: N 4.94.

Tetraacetyl-D-glucopyranosyldimethylhydroquinone. A solution of dimethylhydroquinonylmagnesium bromide was prepared from 3.93 g (0.16 mole) of magnesium and 34.72 g (0.16 mole) of bromodimethylhydroquinone in 120 ml of absolute ether. To this solution was added a solution of 5 g (0.013 mole) of acetochloroglucose in 75 ml of absolute ether. The reaction mixture was stirred for 5 hr on a hot water bath. Further treatment was as usual.

Acetylation yielded 1.2 g (18.8% of theoretical) of a cream-colored crystalline product with an m. p. of 134-135°. The substance was soluble in ether, chloroform, and methyl alcohol and insoluble in water and petroleum ether. Dimethylhydroquinonecarboxylic acid was identified as one of the products of oxidative cleavage by alkaline permanganate. This is the first description of the product.

Found %: C 56.28; H 6.13. $C_{22}H_{28}O_{11}$. Calculated %: C 56.41; H 5.98.

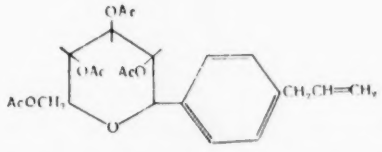
On the basis of the synthesis and the analytical data, the compound is assigned the following structure:



p-Allyltetraacetyl-D-glucopyranosylbenzene. A solution of p-allylphenylmagnesium bromide was prepared from 3.93 g (0.16 mole) of magnesium and 31.52 g (0.16 mole) of p-allylbromobenzene in 70 ml of absolute ether. To this solution was added 5 g (0.013 mole) of acetochloroglucose in 75 ml of absolute ether. The mixture was stirred at room temperature for 1 hr and then for 3 hr on a hot water bath. Further treatment was carried out as usual. There was obtained 1.7 g (28.1% of theoretical) of a white crystalline substance with an m. p. of 88-90°. The material was soluble in the usual organic solvents. Oxidation with alkaline permanganate gave terephthalic acid. The substance decolorized bromine water. This is the first description of the compound.

Found %: C 61.37; H 6.34. $C_{23}H_{28}O_9$. Calculated %: C 61.60; H 6.25.

The structure is represented by the formula:



p-Triacetyl-L-rhamnopyranosylanisole. To a solution of p-anisylmagnesium bromide, prepared from 5.52 g (0.23 mole) of magnesium and 43 g (0.23 mole) of p-bromoanisole in 100 ml of absolute ether, was added a solution

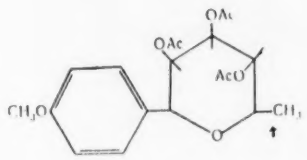
of 8 g (0.023 mole) of acetochlororhamnose in 100 ml of absolute ether. The reaction mixture was stirred for 1 hr at room temperature and then for 3 hr while heating. Further treatment was carried out as usual. Evaporation of the ether left 7.3 g of a thick, viscous substance (74.1% of theoretical).

Recrystallization from isopropyl alcohol gave 2.4 g of a snow-white crystalline substance with an m. p. of 106-107°. The syrup remaining after evaporation of the isopropyl alcohol was not investigated.

Oxidation of the crystalline product gave p-methoxybenzoic acid. The substance was soluble in ether, chloroform, and methyl alcohol and insoluble in water and petroleum ether. This is the first description of the compound.

Found %: C 59.78; H 6.33. $C_{19}H_{24}O_8$. Calculated %: C 60.00; H 6.31.

The structural formula is:



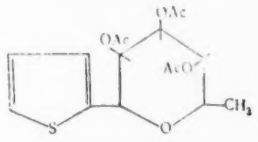
p-L-Rhamnopyranosylanisole. A solution of 1 g of p-triacetyl-L-rhamnopyranosylanisole in 50 ml of absolute methyl alcohol was saturated with dry ammonia and allowed to stand overnight. The sirupy residue remaining after evaporation of the methyl alcohol was washed with ether and recrystallized from benzene. There was obtained 0.4 g (51% of theoretical) of a white crystalline substance with an m. p. of 121.5-123°. It was soluble in water, lower alcohols, and hot benzene and insoluble in ether and petroleum ether. This is the first description of the compound.

Found %: C 61.29; H 7.28. $C_{13}H_{18}O_5$. Calculated %: C 61.41; H 7.08.

α-Triacetyl-L-rhamnopyranosyl thiophene. To a solution of thienylmagnesium iodide, prepared from 3.82 g (0.16 mole) of magnesium and 33.6 of α-iodothiophene in 70 ml of absolute ether, was gradually added 5 g (0.016 mole) of acetochlororhamnose. The usual treatment resulted in 0.92 g (16.1% of theoretical) of a sirup which could not be crystallized. Oxidation of the product with alkaline permanganate gave α-thiophenecarboxylic acid. This is the first description of the compound.

Found %: S 8.64. $C_{16}H_{20}O_7S$. Calculated %: S 8.98.

The following structure has been assigned to the compound:



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ARYLALKYLATION OF ANISOLE WITH STYRENE AND α-METHYLSTYRENE IN THE PRESENCE OF $BF_3 \cdot H_3PO_4$ AND $BF_3 \cdot O(C_2H_5)_2$

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Kiev Polytechnic Institute

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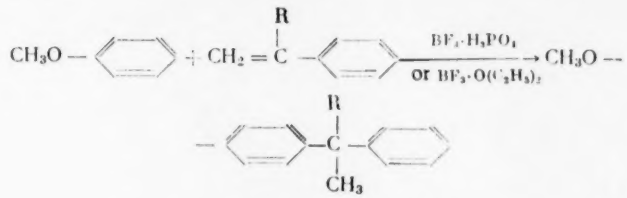
There has been almost no study of arylalkylation of alkyl phenyl ethers with olefins. The reaction of anisole with styrene and with α-methylstyrene in the presence of $BF_3 \cdot H_3PO_4$ or $BF_3 \cdot O(C_2H_5)_2$ as the catalyst was studied in the present work. It was shown that the reaction proceeds mainly according to the scheme:



(R = H or CH_3).

The interaction of anisole with styrene in the presence of either catalyst yields p-methoxyphenylphenylmethylmethane (I). The reaction is accompanied by polymerization of part of the styrene. The most favorable conditions, under which (I) was formed in a yield of 87-88% of theoretical, are the following: molar ratios of anisole, styrene, and catalyst of 5:1:0.3, respectively, and a temperature of 60°.

Anisole reacts with α-methylstyrene to form p-methoxyphenylphenyldimethylmethane (II). The reaction takes place less vigorously than it does with styrene. $BF_3 \cdot O(C_2H_5)_2$ proved to be the most effective catalyst for this reaction. Arylalkylation is accompanied by polymerization to a lesser extent in the presence of boron trifluoride etherate, and the use of this catalyst leads to a higher yield of (II). The yield of (II) was 71% of theoretical with molar ratios of anisole, α-methylstyrene, and $BF_3 \cdot O(C_2H_5)_2$ of 5:1:0.5, a temperature of 60°, and a reaction time of 8.5 hr. A decrease in the reaction temperature to 20-30° decreased the yield of (II) and increased polymerization of the α-methylstyrene to viscous, oily products. The reaction was accompanied by a considerably greater amount of olefin polymerization when it was carried out in the presence of $BF_3 \cdot H_3PO_4$. In this case α-methylstyrene dimer, 1,1,3-trimethyl-3-phenylindane was formed in addition to the viscous polymers. Under certain conditions (a relatively small amount of $BF_3 \cdot H_3PO_4$), the yield of this polymer was 46%, based on the α-methylstyrene. The best conditions, under which (II) was obtained in a yield of 55% of theoretical, were the following: molar ratios of anisole, α-methylstyrene, and $BF_3 \cdot H_3PO_4$ of 4:1:0.2, a temperature of 60°, and a reaction time of 1.5 hr.

The primary arylalkylation products were identified by demethylation to the corresponding aralkylphenols and conversion of the latter to the aralkylphenoxyacetic acids.

EXPERIMENTAL

The anisole was freshly distilled commercial product with a b. p. of 154°, d^{20}_4 0.9908, $n^{20}D$ 1.5183. The styrene was freshly distilled technical styrene with a b. p. of 30°/3 mm, d^{20}_4 0.9047, $n^{20}D$ 1.5420. The α-methylstyrene was separated from by-products of the production of phenol from cumene, and it had a b. p. of 35-40°/2 mm, d^{20}_4 0.9082, $n^{20}D$ 1.5360. The catalysts were prepared as described previously [1].

Arylalkylation of anisole with styrene. The reaction was carried out in a three-neck flask fitted with a stirrer, a thermometer, and a dropping funnel. The anisole and catalyst were placed in the flask, and, with vigorous stirring and with the mixture at the desired temperature, styrene was added from the dropping funnel at a rate of 2.5-4 hr per mole. The styrene used in each experiment amounted to 0.1-0.2 mole, and anisole and catalyst were taken in the appropriate amounts to yield the desired reactant ratios. The reaction began after an induction period of 10-15 min, and it proceeded in a homogeneous medium, since the reagents, catalyst, and products mixed readily forming a light-yellow liquid, the color of which did not change throughout the reaction. After the addition of the calculated amount of styrene, the reaction mixture was stirred for 1 hr at the temperature of the experiment and treated in the usual manner. The unreacted starting material were distilled at atmospheric pressure. The reaction products distilled under vacuum within a range of 3-5°. The oily residue in the distillation flask amounted to 2-7 g. The most characteristic experiments are summarized in Table 1.

TABLE 1. Arylalkylation of Anisole with Styrene

Expt. No.	Molar ratios of anisole, styrene, and $BF_3 \cdot H_3PO_4$	Temp., °C	Reaction time	Yield of p-methoxyphenylphenylmethylmethane, % of theoretical	Oily residue in flask, g
1	5:1:0,3	60	1 h. 45 m.	88,2	5,3
2*	5:1:0,3	60	1 h. 45 m.	87,2	3,1
3	5:1:0,2	60	1 h. 50 m.	81,6	2,2
4	4:1:0,4	60	2 h.	52,4	6,7
5	4:1:0,3	60	1 h. 40 m.	81,1	3,0
6	4:1:0,3	60	1 h. 45 m.	84,9	0,6
7*	4:1:0,3	60	1 h. 45 m.	70,7	4,3
8	4:1:0,2	40	1 h. 45 m.	79,7	2,3
9	4:1:0,2	60	1 h. 50 m.	81,1	4,4

* The experiments were carried out in the presence of $BF_3 \cdot O(CH_2H_5)_2$.

p-Methoxyphenylphenylmethylmethane (I) was transparent liquid with a b. p. of 161-163°/8 mm, d^{20}_4 1.0517, $n^{20}D$ 1.5735; MR_D found, 66.31; calculated 65.79. Literature data [2]: b. p. 183°/17 mm, $n^{26}D$ 1.5680.

p-Hydroxyphenylphenylmethylmethane (III) was prepared by demethylation of (I). A mixture of 15 g of product (I) with 100 ml of HBr and 70 ml of acetic anhydride was heated until it boiled lightly, maintained under these conditions for 45 hr, and then treated in the usual manner [3]. Distillation of the product separated 5.5 g (39.2% of theoretical) of (III). It was a viscous, yellowish liquid. B. p. 133-134°/5 mm, d^{20}_4 1.1142, $n^{20}D$ 1.5885; MR_D: found 59.67, calculated 60.06. Literature data [4]: b. p. 122-126°/1.5 mm, $n^{23}D$ 1.5904. In addition to the (III), 0.5 g of phenol and a small amount of an unidentified hydrocarbon with a b. p. of 230°/4 mm, $n^{20}D$ 1.6011, were also separated from the demethylation products. Consequently, demethylation of (I) is accompanied by partial cleavage.

p-(α-Methylbenzyl)phenoxyacetic acid (IV). This was prepared from (III) and monochloroacetic acid; the yield was 83.7% of theoretical. The white plates melted at 97-99°. Mol. wt.: found 256.7 and 259.0. $C_{16}H_{16}O_3$. Calculated 256.3.

Arylalkylation of anisole with α-methylstyrene. The reaction was carried out in the same manner as with styrene. The mixture remained a homogeneous liquid with a light yellow color throughout the process. When boron trifluoride etherate was used in certain experiments, the anisole and α-methylstyrene were placed in the reaction flask, and the catalyst was added dropwise from the dropping funnel. The amount of α-methylstyrene taken for each experiment was 0.1 mole, and anisole and catalyst were used in the appropriate amounts to give the desired reactant ratios. The oily residue in the distillation flask varied from 0.8 to 4.4 g. Even in the first distillation of the alkylate, the arylalkylation product (II), distilled within a 1-2° range. When $BF_3 \cdot H_3PO_4$ complex was used as the catalyst, 0.2 mole of α-methylstyrene was used along with the appropriate amounts of anisole and catalyst. In contrast to the experiments in which boron trifluoride etherate catalyst was used, in this case arylalkylation was accompanied by considerable dimerization of the α-methylstyrene to 1,1,3-trimethyl-3-phenylindane. During fractionation of the alkylate, the latter compound distilled together with the primary arylalkylation product, p-methoxyphenylphenyldimethylmethane, within a 2-5° range, and was separated from it by fractional crystallization. As in the experiments

with $BF_3 \cdot O(C_2H_5)_2$ catalyst, an oily, viscous mass remained in the distillation flask. The data from certain experiments are summarized in Table 2.

TABLE 2. Arylalkylation of Anisole with α-Methylstyrene

Expt. No.	Molar ratios of anisole, α-methyl styrene, and catalyst	Temp. °C ± 2°	Reaction time, hours	Yield of reaction products, % of theoretical		Oily residue in flask, g
				p-Methoxyphenylphenyldimethylmethane	1,1,3-Trimethyl-3-phenylindane	
			$BF_3 \cdot O(C_2H_5)_2$ catalyst *			
1	7:1:0,5	40	8,0	62,4	Traces	0,8
2	5:1:0,5	40	6,5	67,7	"	1,0
3	5:1:0,5	60	8,5	70,8	"	0,8
4**	5:1:0,5	60	8,0	68,6	"	2,2
5	5:1:0,3	20	7,0	35,4	"	4,4
6	5:1:0,3	30	8,0	50,0	"	3,5
7	4:1:0,3	20	6,0	26,1	"	4,2
8	4:1:0,3	30	5,0	31,1	"	3,5
			$BF_3 \cdot H_3PO_4$ catalyst			
9	5:1:0,5	60	2,0	50,3	8,4	5,0
10	5:1:0,2	60	1,5	41,1	27,8	3,0
11	4:1:0,4	60	1,5	44,6	19,9	5,7
12	4:1:0,3	40	2,0	44,6	34,7	5,9
13	4:1:0,3	60	1,5	48,6	16,9	6,3
14	4:1:0,2	40	1,5	50,2	22,3	7,2
15	4:1:0,2	60	1,5	54,8	15,6	5,4
16	4:1:0,1	60	1,5	24,3	45,7	2,0
17	3:1:0,2	60	1,5	29,6	32,2	4,2
18	1:1:0,2	60	1,5	53,5	38,1	2,7

* A. I. Kosyakov took part in carrying out the experiment.

** The catalyst was added dropwise to a mixture of anisole and α-methylstyrene in these experiments.

p-Methoxyphenylphenyldimethylmethane (II) is a colorless liquid with the odor of anisole. It has a b. p. of 154-156°/3 mm, d^{20}_4 1.0424, $n^{20}D$ 1.5698; MR_D: found 70.89, calculated 71.52. Mole wt.: found 226.0, calculated for $C_{16}H_{18}O$, 226.1. Literature data [5]: b. p. 198-199°/25 mm, d^{25}_4 1.0367, $n^{25}D$ 1.5685.

p-Hydroxyphenylphenyldimethylmethane (V) was prepared by demethylation of (II). A mixture of 10 g of compound (II), 100 ml of HBr, and 70 ml of acetic anhydride was heated until it boiled lightly and held at this point for 45 hr. After the appropriate treatment and distillation, the yield of (V) was 3 g or 32.2% of theoretical. The white crystals melted at 72-73°, which is in agreement with the m. p. reported in the literature [6].

p-(α,α-Dimethylbenzyl)phenoxyacetic acid (VI). To a solution of 1 g of compound (V) in 5 ml of 33% NaOH was added 1.5 g of monochloroacetic acid, and the mixture was heated on a water bath for one hr. After being cooled to room temperature, the products were mixed with water, acidified, and extracted with ether. The ether extract was washed with a 5% solution of soda and acidified with HCl. The precipitated crystals of (VI) were separated by filtration and dried. The yield of (VI) was 0.7 g or 55.1% of theoretical. The m. p. was 117-118° (from hot water). Literature data [5]: m. p. 117°.

1,1,3-Trimethyl-3-phenylindane was obtained in the form of white crystals. The m. p. was 53-54°. A mixture with a pure sample showed no depression of the melting point. Literature data [7]: m. p. 52°.

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POLYMORPHISM IN CRYSTALLINE POLYPROPYLENE

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There is no longer any reason to doubt that any crystalline polymer can be crystallized under specific conditions to yield single crystals [1-8]. Since the process of crystal formation is a complex multistep process, which has been traced in detail for polyethylene, we may well expect the appearance of a large variety of morphological forms, and these are the subject of the present investigation.

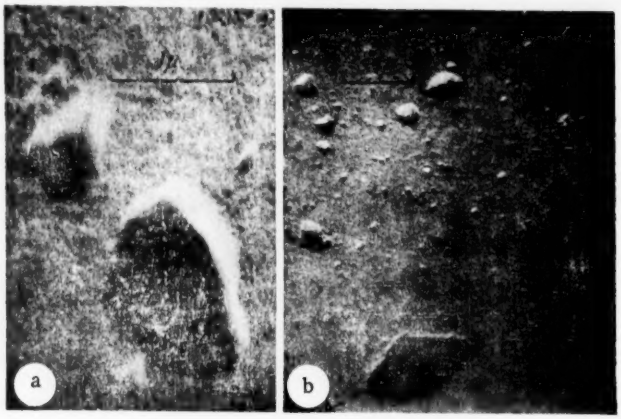


Fig. 1. Single crystal of polypropylene. a) Crystallized from an 0.01% solution in decalin, 23,000 ×; b) crystallized from an 0.01% solution in decalin, 13,000 ×.

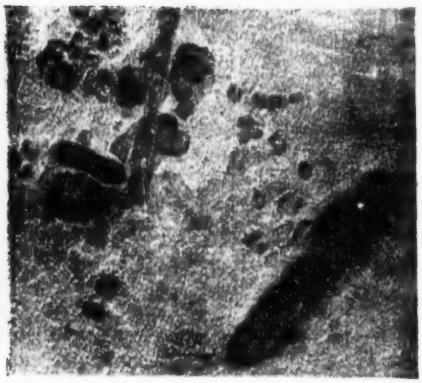
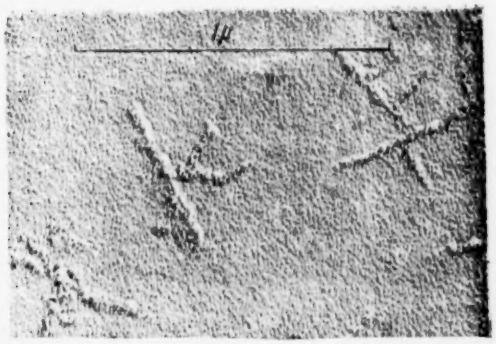


Fig. 2. Polypropylene crystallized from an 0.005% solution in decalin, 350,000×.

Fig. 3. Polypropylene crystals crystallized from an 0.1% solution in xylene, 88,000 ×.

The polymer selected for the present investigation was a high-molecular-weight stereoregular polypropylene

(Mole wt. 100,000). Decalin and xylene solutions of the polymer varying in concentration from 0.001 to 0.1% were heated at 10-15° below the boiling point of the solvent and then slowly cooled (over a period of 2 weeks) to room temperature. The resulting transparent suspension was deposited on collodion film, shadowed to increase contrast, and examined with a GEM-5G electron microscope. Electron diffraction patterns obtained from single crystals (Figs. 1a, 1b, 2, and 3) were sharp, and the reflections disappeared under the electron beam, which apparently destroyed the ability of the sample to diffract without simultaneously affecting its form.



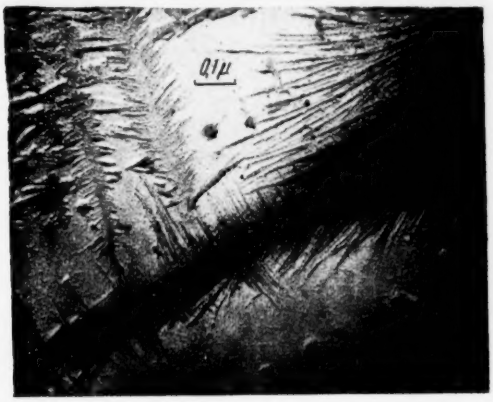


Fig. 4. Polypropylene. a) crystallized from an 0.001% solution in xylene, 60,000 ×; b) crystallized from an 0.01% solution in xylene, 68,000 ×.

In the present investigation of polypropylene, we were able to observe for the first time for any polymer such a variety of morphological forms as elongated rods with a length of up to 5 μ, equilateral triangles, hexagonal crystals, crystals in the form of "snow flakes," large crystals with well-formed lateral faces, and rhombohedrons, which are very common in polymers.

Intermediate crystalline forms were obtained by a change in the crystallization conditions (temperature, concentration, cooling rate). When the concentration was low (less than equal to 0.001%) and the temperature was close to the boiling point of the solvent, asymmetric forms with dimensions up to 0.5 μ (Fig. 4a) were formed, and with a slight increase in concentration or a decrease in temperature, these became longer to form linear structural units (threads). These threads were especially long when the solvent was decalin. Further changes in the process led to elongated crab (photograph not shown), acicular, and dendritic (Fig. 4b) forms with transverse ordering of these linear structural units. These preliminary data force us to consider that the Keller mechanism of the formation of crystal structures with layers of faces is apparently not the sole mechanism of polymer crystallization. This will be discussed in a subsequent communication.

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COMPLEXES OF POLYACROLEIN WITH SALTS OF HEAVY METALS

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Ethers, esters, ketones, and diketones are known to form rather stable complexes with salts of certain heavy metals [1]. This ability is comparable to the ability of oxygen-containing organic molecules to form oxonium compounds. In the series

$$R_2O < R-OH < R-COOH < RCOOR' < RCOR' < R-C\begin{matrix}O\\H\end{matrix}$$

the ability to form oxonium salts increases from left to right [2, 3].

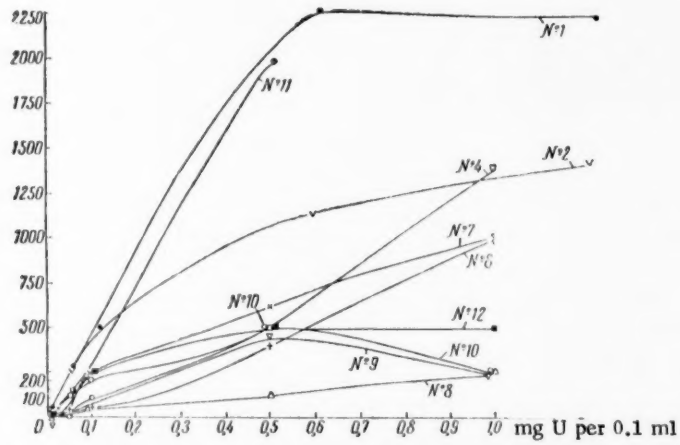

Fig. 1. Dependence of the amount of uranium extracted (in 10^{-6} g/g) on the concentration of the original solution. Curve numbers correspond to the sample numbers in Table 1.

Such compounds as diethyl ether, thenoyltrifluoroacetone, methyl isobutyl ketone, acetylacetone, dibenzoylmethane, etc., are used to separate uranium from its solutions by extraction [1]. A very characteristic composition of uranyl nitrate complexes is two molecules of the addend for each molecule of the inorganic salt. There are indications [4, 5] that the ability of uranyl nitrate to form coordination complexes and the associated solubility of uranyl nitrate in organic oxygen-containing solvents decreases with an increase in the ratio of the number of C atoms to the number of O atoms in the organic molecule. The mechanism of the extraction of heavy metal salts by low-molecular-weight organic substances has been discussed by Kuznetsov [6] and Vdovenko [1].

The literature contains no indication that high-molecular-weight synthetic oxygen containing products are capable of forming coordination complexes with heavy metal salts. We have found that samples of powdered

polyacrolein, prepared under various conditions, possess a very distinct ability to form coordination complexes with heavy metal salts. Of the numerous salts investigated, uranyl nitrate possesses the most clearly expressed capability toward this type of reaction. Lead, cobalt, manganese, copper, nickel, and iron salts did not yield stable complexes within the pH range investigated.

TABLE 1. Methods of Preparation and Some Properties of the Polyacrolein Samples

Sample No.	Method of preparation	Content of aldehyde groups by oxime formation, mole %	Amount of uranium extracted, 10^{-6} g/g
1	In aqueous solution in the presence of $K_2S_2O_8 + AgNO_3$	74	2305
2	Same in the presence of $K_2S_2O_8 + (NH_4)_2Fe(SO_4)_2$	65	1450
3	Same in the presence of $K_2S_2O_8 + Na_2S_2O_3$	30	1000
4	Disacryl	60	1400
7	Spontaneous polymerization in an ampoule in the presence of hydroquinone	5-7	1000
8	Mass polymerization in the presence of BF_3 at a temperature of from 0° to −20°	None	250
9	Same with BF_3 in the presence of traces of water at −20°	None	450
10	In methylene chloride solution in presence of BF_3 at −20°	None	500
11	In benzene solution in the presence of metallic sodium	22	2000
12	Mass polymerization in the presence of butyllithium at room temperature	9	560

TABLE 2. Dependence of the Distribution Coefficient ($K \cdot 10^{-5}$) on Uranium Concentration of the Solution

Uranium concentration, mg/ml	Polyacrolein sample									
	No. 1	No. 2	No. 3	No. 4	No. 7	No. 8	No. 9	No. 10	No. 11	No. 12
0.001	4803	4712	2564	1253	2564	0	0	0	2040	250
0.005	4803	4712	551	2459	–	502	503	–	2564	122
0.01	4393	4167	503	2145	2564	502	756	1010	2564	256
0.05	3950	1936	806	1010	1265	2506	908	1010	2060	1010
0.10	1942	1213	1010	1419	1010	1506	2506	2506	1522	–

Table 1 presents information on the methods of preparation and on certain properties of the sample of polyacrolein investigated in the present work. Figure 1 presents data on the extraction of uranyl nitrate from aqueous solutions under static conditions, and Fig. 2 shows the relationship between the amount of uranium extracted and the uranium concentration in the original solution. The relationship between the apparent distribution coefficient for uranium between the organic and aqueous phases and the concentration of the salt is shown in Table 2.

Polyacrolein has the most favorable ratio of number of carbon atoms to number of oxygen atoms for the formation of coordination complexes.

The greatest capability for the extraction of uranium from aqueous solutions was possessed by polyacrolein samples prepared by the polymerization of acrolein in aqueous solution in the presence of potassium persulfate–silver nitrate and potassium persulfate–Mohr's salt redox systems. The disacryl sample was less able to extract uranyl nitrate from solution, as was the polyacrolein prepared with a potassium persulfate–sodium thiosulfate system.

The polyacrolein samples prepared in the presence of boron trifluoride at low temperature and the sample prepared in the presence of butyllithium showed the least ability toward extraction. There does exist a definite relationship between the content of aldehyde groups, as determined by the oxime formation method, and the ability to extract uranium from aqueous solutions (see Table 2).

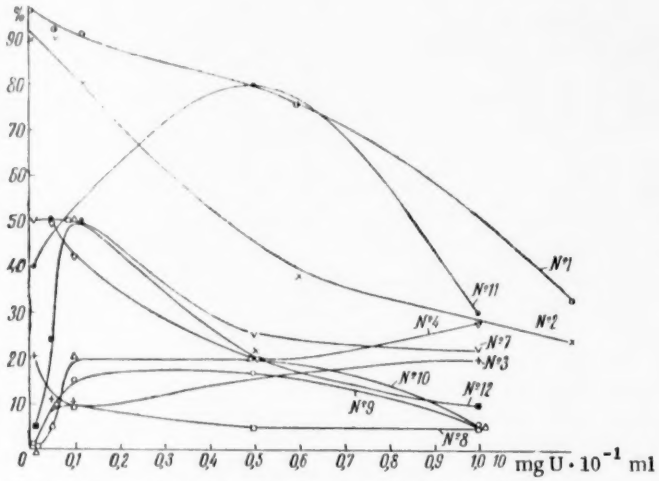

Fig. 2. Dependence of percentage uranium extraction on concentration of the original solution.

The extraction of uranium takes place over a narrow pH range of from 3 to 4. The percentage extraction decreases sharply outside this range. The distribution coefficients for the various polyacrolein samples varied from 0.005025 to 0.04803, i.e., by a factor of ten.

The uranium absorbed by polyacrolein can be quantitatively returned to solution by treatment with a dilute solution of hydrochloric acid.

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ORGANOTIN AND ORGANOLEAD DERIVATIVES OF SOME NITROGEN-CONTAINING ACIDS

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We have previously studied [1, 2] the synthesis and properties of organotin and organolead esters of methacrylic acid, which we have chosen to call organotin and organolead methacrylates; these esters have the general structure $R_3SnOOCC(CH_3) = CH_2$, $R_2Sn[OOCC(CH_3) = CH_2]_2$, and $(C_6H_5)_2Pb[OOCC(CH_3) = CH_2]_2$. Polymers of these compounds and copolymers with a number of unsaturated monomers have also been prepared [1, 2].

It is known that certain nitrogen-containing acids, for example, α-alanine, p-aminobenzoic acid, nicotinic acid (β-pyridinecarboxylic acid, vitamin PP), isocinchomeronic acid (2,5-pyridinedicarboxylic acid), orotic acid (4-uracilcarboxylic acid, a vitamin of the B_{13} group), and uracilacetic acid play an exceptionally important role in the life processes of organisms and plants. Orotic acid, which plays a part in the construction of nucleic acids and which is also a growth factor, has not been investigated to any extent [3]. A method for its preparation is given below. The method is based on the one proposed by Hilbert, but it differs in that in place of potassium ferricyanide, we used chromic acid, which considerably facilitates synthesis of the acid. On the other hand, such organotin compounds as the organotin hydroxides (R_3SnOH), the acetylstannanes ($R_3SnOOCCH_3$), and alkylstannyl esters of nicotinic acid ($R_3SnOOCC_5H_4N$) [8], possess pesticidal properties and suppress the growth of lower forms of life – moles, fungi, etc.

We have investigated organotin and organolead esters of the above nitrogen-containing acids with the aim of synthesizing biologically active heteroorganic compounds having a favorable physiological action on organisms. The corresponding derivatives of α-alanine, nicotinic acid, isocinchomeronic acid, p-aminobenzoic acid, orotic acid, and uracilacetic acid were prepared by the reactions:

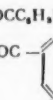
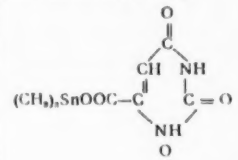
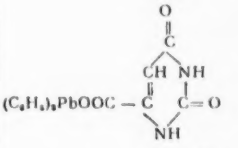
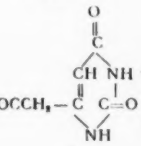
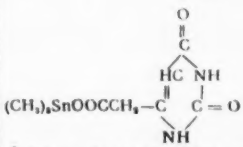
$$R_3MOH + R'COOH \rightarrow R_3MOOCR' + H_2O;$$
$$2R_3MOH + HOOCR''COOH \rightarrow R_3MOOCR''COOMR_3 + 2H_2O;$$
$$R_2MO + 2R'COOH \rightarrow R_2M(OOCR')_2 + H_2O;$$
$$R_3MOMR_3 + 2R'COOH \rightarrow 2R_3MOOCR' + H_2O \text{ where } M = Sn, Pb.$$

The interaction of triphenyllead hydroxide with nicotinic and uracilacetic acid takes place in a different manner. In these cases, diphenylplumbylene esters of the respective acids are formed, as in the interaction with methacrylic acid [2]. In addition, elimination of a phenyl group also occurs:

$$(C_6H_5)_3PbOH + 2C_5H_4NCOOH \rightarrow (C_6H_5)_2Pb(OOCC_5H_4N)_2 + C_6H_6 + H_2O.$$
$$(C_6H_5)_3PbOH + 2HOOCCH_2C_4H_3N_2O_2 \rightarrow (C_6H_5)_2Pb(OOCCH_2C_4H_3N_2O_2)_2 + C_6H_6 + H_2O.$$

We have previously established [8] that these organotin and organolead compounds also possess pesticidal properties, which depend to a great extent on the nature of the alkyl groups in the molecule. Thus, organotin derivatives of nicotinic acid and alanine suppress the growth of such cultures as Escherichia coli, Streptococcus faecalis, and Lactobacillus casei, even when present in very small amounts.

All of these organotin and organolead compounds are crystalline materials, difficultly soluble in water, and readily soluble in organic solvents. The trimethylstannyl esters of α-alanine and orotic acid are soluble in water and difficultly soluble in organic solvents.

Prep. No.	Compound	M. p., °C	Yield, %	Analysis, %							
				C		H		N		Sn	
				found	calc.	found	calc.	found	calc.	found	calc.
10	$(CH_3)_3SnOOC$	188—190	69,1	37,72 38,07	37,81	4,70 4,81	4,85	5,17 5,19	4,89	41,13 41,25	41,52
4	$(C_2H_5)_3SnOOC$	108—110	85,6	43,91 43,67	43,93	5,95 5,90	5,93	4,64 4,43	4,27	35,78 35,81	36,19
3	$(n\text{-}C_4H_9)_3SnOOC$	90—92	79,3	49,00 49,15	48,71	7,02 7,04	6,81	3,74 3,60	3,71		
5	$(C_2H_5)_2Sn(OOC$ $)_2$	211—212	85,7	45,34 45,53	45,65	4,21 4,20	4,31	6,25 6,32	6,65	28,00 27,89	28,20
2	$(n\text{-}C_4H_9)_2Sn(OOC$ $)_2$	156—158	82,4	47,59 47,83	48,14	4,81 4,69	4,94	6,13 6,17	6,24	26,15 26,04	26,44
6	$(C_2H_5)_2SnOOCC_6H_4NCOOSn(C_2H_5)_2$	263	50,1	39,25 39,20	39,56	5,64 5,88	5,76	2,58 2,61	2,42	40,95 41,00	41,15
7	$(n\text{-}C_4H_9)_2SnOOCC_6H_4NCOOSn(C_4H_9\text{-}n)_2$	144—145	31,3	45,18 45,00	45,43	6,61 6,85	6,86	2,21 2,21	2,12	35,53 35,68	35,91
12	$(C_6H_5)_2Pb(OOC$  $)_2$	200	71,1	47,76 47,80	47,59	3,07 3,17	2,99	10,52 10,63	10,57		
16	$(CH_3)_2SnOOCCH(NH_2)CH_3$	215	40,0	28,47 28,32	28,61	5,83 5,78	6,00	5,35 5,45	5,55	46,93 46,87	47,12
41	$(CH_3)_2SnOOCC_6H_4NH_2\text{-}p$	258,5— —259,5 (de- comp.)	30,0	39,87 39,91	40,04	4,87 4,98	5,04	4,51 4,18	4,67	39,12 39,02	39,55
33	$(CH_3)_2SnOOC$ 	302—303	54,1	30,18 30,09	30,13	3,69 3,60	3,79	9,12 9,00	8,78	36,87 36,93	37,22
34	$(C_6H_5)_2PbOOC$ 	350	60,25	46,64 46,40	46,52	3,41 3,43	3,06	5,00 5,03	4,72		
35	$(C_6H_5)_2Pb(OOCCH_2$  $)_2$	330 (de- comp.)	60,0	40,59 40,71	41,19	2,86 2,83	2,88	7,35 7,48	8,00		
32	$(CH_3)_2SnOOCCH_2$ 	345 (de- comp.)		32,17 32,21	32,47	3,87 3,92	4,23	8,11 8,08	8,41	35,00 35,08	35,66
45	$(iso\text{-}C_4H_9)_2Sn(OOCC_6H_4NH_2\text{-}p)_2$	181—182		52,36 52,35	52,30	6,06 6,09	5,98	5,51 5,52	5,54	23,40 23,57	23,49

EXPERIMENTAL

Trimethylstannyl ester of nicotinic acid, $(CH_3)_3SnOOCC_5H_4N$ (10). In a three-neck flask fitted with a stirrer and reflux condenser was placed 5.4 g (0.03 mole) of trimethyltin oxide [1], 3.7 g (0.03 mole) of nicotinic acid (m. p. 234-237°), and 40 ml of water. The mixture was heated at the boiling point for 1.5-2 hr and then allowed to stand overnight. The crystals were separated by filtration on a glass filter and washed several times with hot water. The yield of nicotinic acid trimethylstannyl ester was 5.9 g (69.1% of theoretical, calculated on the trimethyltin hydroxide). After recrystallization from benzene, the product melted at 188-190°. The substance was difficultly soluble in water and soluble in the common organic solvents.

Tri-n-propylstannyl ester of nicotinic acid, $(n\text{-}C_3H_7)_3SnOOCC_5H_4N$ (3). The nicotinic acid, 2.4 g (0.02 mole), was placed in a flask and dissolved by heating in 30 ml of water; 2.5 g (0.01 mole) of bis(tri-n-propyltin) oxide (b. p. 148° at 3 mm, $n^{20}D$ 1.4915) [1] was then added from a dropping funnel. The reaction mixture was heated, with stirring, at 70° for 2 hr and allowed to stand overnight. The resulting precipitate was separated by filtration and washed with several portions of hot water. The yield of nicotinic acid tri-n-propylstannyl ester was 2.9 g [79.3% of theoretical, calculated on the bis(tri-n-propyltin) oxide]. After recrystallization from benzene, the product melted at 90-92°.

Dipropylstannylene ester of nicotinic acid, $(n\text{-}C_3H_7)_2Sn(OOCC_5H_4N)_2$ (2). To a three-neck flask was charged 2.2 g (0.01 mole) of di-n-propyltin oxide $(n\text{-}C_3H_7)_2SnO$, prepared by hydrolysis of tri-n-propyltin bromide [1], 20 ml of water, and 2.7 g (0.02 mole) of nicotinic acid. The reaction mixture was heated at the boiling point for a period of 20 minutes. Solution of the material set in during this period, and then a crystalline precipitate began to form. This was separated by filtration, washed with several portions of hot water, and dried under vacuum. There was obtained 3.7 g of nicotinic acid di-n-propylstannylene ester. After repeated recrystallization from chloroform, the product melted at 156-158°.

The trialkylstannyl and dialkylstannylene esters of nicotinic acid shown in the table were synthesized in a similar manner. These substances were white crystalline materials, difficultly soluble in water, and readily soluble in benzene, chloroform, and other organic solvents.

Diphenylplumbylene ester of nicotinic acid, $(C_6H_5)_2Pb(OOCC_5H_4N)_2$ (12). To a flask were charged 20 ml of alcohol and 4.6 g (0.01 mole) of triphenyllead hydroxide, prepared by hydrolysis of triphenyllead chloride with alcoholic alkali [2]. After the triphenyllead hydroxide had dissolved, 1.2 g (0.01 mole) of nicotinic acid was added, and the reaction mixture was heated at the boiling point for a period of 1.5-2 hr. A crystalline precipitate formed toward the end of this period. It was separated by filtration and washed with hot water. The substance (m. p. 200°) proved to be nicotinic acid diphenylplumbylene ester; it was readily soluble in benzene and chloroform, sparingly soluble in alcohol, and insoluble in water.

Bis(triethylstannyl) ester of isocinchomeronic acid, $(C_2H_5)_3SnOOCC_5H_3NCOOSn(C_2H_5)_3$ (6). A mixture of 2.2 g (0.01 mole) of triethyltin hydroxide (or, alternatively, bis(triethyl)tin oxide [1]), 35 ml of water, and 0.8 g (0.005 mole) of isocinchomeronic acid (m. p. 245°) in a three-neck flask was heated at the boiling point for 3-4 hr. During this time, the acid dissolved, and flocculent crystals formed. The crystalline product, isocinchomeronic acid bis(triethylstannyl) ester, was obtained by recrystallization from chloroform. It was difficultly soluble in organic solvents and insoluble in water.

Diisobutylstannylene ester of p-aminobenzoic acid (diisobutylstannylene di-p-aminobenzoate), $(iso\text{-}C_4H_9)_2 \cdot Sn(OOCC_6H_4NH_2)_2$ (45). A mixture of 0.67 g (0.005 mole) of diisobutyltin oxide,* 0.62 g (0.005 mole) of p-aminobenzoic acid, and 50 ml of water was placed in a flask fitted with a reflux condenser and heated at the boiling point for 5 hr. On the following day, the precipitate was filtered, boiled with 25 ml of water to remove traces of p-aminobenzoic acid, and, after filtration, washed with several portions of hot water. The reaction product was then recrystallized from ether – when the ether solution was evaporated to ½ its volume, a flocculent white precipitate of diisobutylstannylene di-p-aminobenzoate (m. p. 181-182°) formed. The substance was soluble in organic solvents and insoluble in water.

* Diisobutyltin oxide, $(iso\text{-}C_4H_9)SnO$, is a white, amorphous substance, which is infusible, decomposing when heated in a flame. It is soluble in alcohol, acetone, and chloroform, difficultly soluble in ether, and insoluble in water. It may be prepared by hydrolysis of triisobutyltin bromide, $(iso\text{-}C_4H_9)_3SnBr$ (b. p. 120-123°/5 mm, $n^{20}D$ 1.5072, d^{20}_4 1.3780), and also by hydrolysis of diisobutyltin dibromide [1].

Orotic acid, $C_4N_2H_3O_2COOH$. To an oxidizing mixture of 8.7 g of sodium dichromate, 8.7 ml of H_2SO_4 (d^{20}_4 1.83), and 43 ml of water was added portionwise 3.5 g of uracilacetic acid [5, 6]. The reaction mixture was heated at the boiling point for 5 min. The resulting precipitate was separated by filtration. There was obtained 2.1 g of a yellowish, finely crystalline substance (m. p. 345°), from which orotic acid monohydrate with a m. p. of 300° (melted with decomposition) was obtained by recrystallization from water. The yield was 66% of theoretical.

Found %: C 34.73, 34.66; H 3.71, 3.62; N 16.00, 15.93. $C_5H_4N_2O_4 \cdot H_2O$. Calculated %: C 34.46; H 3.47; N 16.15.

The orotic acid crystallized as rhombic plates. It was soluble in hot water (1:70 at 100°), insoluble in the common organic solvents, and difficultly soluble in ether.

Diphenylplumbylene ester of uracilacetic acid, $(C_6H_5)_2Pb(OOCCH_2C_4H_3N_2O_2)_2$ (35). A mixture of 3.4 g (0.02 mole) of uracilacetic acid and 2.3 g (0.005 mole) of triphenyllead hydroxide was dissolved in 60 ml of hot ethyl alcohol, and the solution was heated at the boiling point for 5 hr. The precipitate was separated by filtration, treated several times with hot water and then with several portions of hot alcohol, and dried to constant weight. There was obtained 2.1 g (60% of theoretical, calculated on the triphenyllead hydroxide) of a white substance with an m. p. of 330° (sintered and decomposed). This material was uracilacetic acid diphenylplumbylene ester.

Trimethylstannyl ester of orotic acid, $(CH_3)_3SnOOCC_4H_3N_2O_2$ (33). A mixture of 0.54 g (0.003 mole) of trimethyltin hydroxide, 0.47 g (0.003 mole) of orotic acid, and 35 ml of water was placed in a flask. The reaction mixture was heated at the boiling point for 12 hr. The aqueous solution was then evaporated to 1/7 its original volume. This caused precipitation of white acicular crystals of the trimethylstannyl ester of orotic acid. The ester was insoluble in the common organic solvents and difficultly soluble in water.

1. Organotin and organolead esters of amino acids (α-alanine and p-aminobenzoic acids), pyridine acids (nicotinic and isochinchomeronic acids), and pyrimidine acids (orotic and uracilacetic acids) were synthesized, and their properties were investigated. It was established that these compounds are pesticides with respect to a number of microorganisms.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

SYNTHESIS OF SOME COMPOUNDS WITH TWO ADJACENT THREE-MEMBERED RINGS

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Original article submitted February 25, 1961

Compounds containing two three-membered rings in the molecule are relatively few, only the following being described in the literature: one dicarboxylic acid and its ester [1], two alicyclic ketones [2,3], one unsaturated ketone [4, 5], two nitroketones [6, 7], nine alcohols, and eight hydrocarbons. Such a small number of these compounds is due to the absence of simple and reliable methods for their synthesis, and it is for this reason that this field of organic chemistry has received but little study in spite of the fact that the chemical and physical properties of the compounds are unusual. Starting with isopropenylcyclopropane, we have synthesized five compounds containing two three-membered rings in the molecule. One of the compounds, the ethyl ester of a dicarboxylic acid, was obtained in about 60% yield of the reaction of diazoacetic acid with isopropenylcyclopropane. This indicates that the double bond in isopropenylcyclopropane is more reactive then the double bond in alkenes [8].

Dimethyl(2-methyl-2-cyclopropyl)cyclopropylcarbinol was prepared by the reaction of the ethyl ester of 2-methyl-2-cyclopropylcyclopropanecarboxylic acid with methyllithium.

The interaction of the ethyl ester of 2-methyl-2-cyclopropylcyclopropanecarboxylic acid and CH_3MgCl gave a mixture of alcohols. Judging from the Raman spectrum, isomerization products of dimethyl(2-methyl-2-cyclopropyl)cyclopropylcarbinol – unsaturated alcohols – predominated in this mixture [characteristic double bond frequency at 1652(10)cm^{-1}].

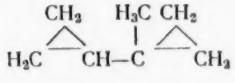
A similar isomerization of a three-membered ring during the preparation of alcohols by Grignard reaction was encountered for the first time during our synthesis of a tertiary alcohol by the action of CH_3MgBr on the ethyl ester of 2,2,3,3-tetramethylcyclopropanecarboxylic acid [9]. Substitution of CH_3MgCl for CH_3MgBr in this case permitted us to obtain the alcohol uncontaminated by unsaturated alcohols. Evidently dimethyl(2-methyl-2-cyclopropyl)cyclopropylcarbinol, which has a still more complex structure, readily isomerizes even in a weakly acid medium at 35°.

Raman spectra* were obtained for all the compounds prepared, and these showed that in none of the remaining cases were there present impurities with a double bond.

EXPERIMENTAL

Isopropenylcyclopropane. This compound was prepared by dehydration of dimethylcyclopropylcarbinol in the presence of 0.01 wt. % H_2SO_4 (100%). The hydrocarbon boiled at 70° at 759 mm, $n^{20}D$ 1.4257, D^{20}_4 0.7509 (the literature [10] reports: b. p. 70.5° at 760 mm, $n^{20}D$ 1.4255, D^{20}_4 0.7513).

1-Methyl-1-cyclopropylcyclopropane



To 16.3 g of Zn/Cu in 165 ml of absolute ether was added 53.6 g of methylene iodide and 0.15 g of iodine. The mixture was heated for 30 min; 33 g of isopropenylcyclopropane was then added dropwise over a period of 1 hr, and heating was continued for 25 hr. The mixture was then treated with 5% aqueous solution of HCl and then with potassium carbonate solution, dried, and distilled. There was obtained 7 g (37%, based on the methylene iodide taken for the reaction) of 1-methyl-1-cyclopropylcyclopropane with a b. p. of 88-92° at 758 mm. After distillation

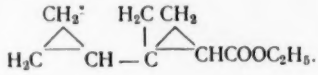
* The spectra were taken by G. K. Galvoronskaya, our co-worker in the optical group of the Laboratory of Hydrocarbon Chemistry.

over metallic sodium, the hydrocarbon had a b. p. of 88-89.5° at 762 mm, D^{20}_4 0.7826, $n^{20}D$ 1.4221 MR_D: found 31.23, calculated 31.64.

Found %: C 87.60, 87.63; H 12.71, 12.42. C_7H_{12}. Calculated %: C 87.42; H 12.57.

Raman spectrum in cm^{-1}: 263(2), 325(2) 365(0), 395(0), 432(1), 455 (1), 481(2), 586(0), 639(5), 745(0), 774(1), 818(0), 831(3), 853(3), 898(1), 933(3), 948(3), 971(0), 1071(0), 1030(1), 1044(0), 1070(1), 1103(1), 1114(1), 1165(0), 1195(8), 1235(1), 1257(1), 1298(0), 1319(2b), 1382(1b), 1427(1b), 1458(1b), 2873(2), 2900(0), 2925(2), 2940(2b), 3002(10b), 3075(3b).

Ethyl ester of 2-Methyl-2-cyclopropylcyclopropanecarboxylic Acid



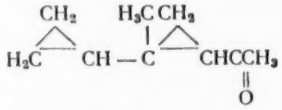
A mixture of 200 g of isopropenylcyclopropane and 4 g of $CuSO_4$ was placed in a flask fitted with a reflux condenser, a dropping funnel, and a stirrer. The mixture was heated to boiling, and a solution of 38.8 g of diazoacetic ester in 32 g of isopropenylcyclopropane was added dropwise. When addition of the solution was complete, the mixture was heated for an additional 30 min, cooled, and filtered from $CuSO_4$; the excess hydrocarbon was distilled. The residue was distilled under vacuum from a Claisen flask, and was then redistilled in a fractionating column with an efficiency of 18 theoretical plates. There was obtained 34 g (59.6%, based on the diazoacetic ester taken for the reaction) of the ethyl ester of 2-methyl-2-cyclopropylcyclopropanecarboxylic acid with a b. p. of 83° at 11 mm, D^{20}_4 0.9613, $n^{20}D$ 1.4513 MR_D: found 4714, calculated 47.34.

Found %: C 71.20, 71.40; H 9.65, 9.72. $C_{10}H_{16}O_2$. Calculated %: C 71.39; H 9.58.

Raman spectrum in cm^{-1}: 265(0b), 316(1b), 355(2b), 390(1), 423(1), 476(1b), 523(1b), 586(1), 618(1), 638(8), 760(7b), 775(1b), 818(5b), 832(4b), 845(6), 859(5), 898(3), 932(3), 945(4b), 962(3b), 1013(2b), 1045(3b), 1072(1), 1096(2b), 1115(3b), 1171(2b), 1195(10), 1244(3b), 1300(4b), 1355(1), 1384(5), 1405(5), 1428(3), 1448(5b), 1468(6b), 1724(6), 2960(1b), 3005(10b), 3075(5b).

2-Methyl-2-cyclopropylcyclopropanecarboxylic acid. This was prepared by saponification of its ethyl ester by heating with a 20% aqueous-alcoholic solution of KOH for 15 hr; b. p. 120° at 11 mm, D^{20}_4 1.0328, $n^{20}D$ 1.4710 MR_D: found 37.93, calculated 37.92.

Methyl 2-Methyl-2-cyclopropylcyclopropyl Ketone

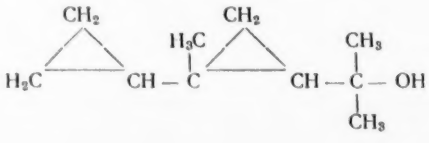


CH_3Li was prepared from 4.5 g of metallic lithium and CH_3Cl in 200 ml of absolute ether. The CH_3Li was heated to 35°, and a solution of 14 g of 2-methyl-2-cyclopropylcyclopropanecarboxylic acid in an equivalent volume of ether was added. The mixture was heated on a water bath for 9 hr and then decomposed with water. The ether solution was dried with solid KOH and distilled. There was obtained 4 g of methyl 2-methyl-2-cyclopropylcyclopropyl ketone. The yield was 29%. B. p. 76-77° at 12 mm, D^{20}_4 0.9047, $n^{20}D$ 1.4588 MR_D: found 41.74, calculated 41.07.

Found %: C 77.68, 77.90; H 10.78, 10.51. $C_9H_{14}O$. Calculated %: C 78.21; H 10.21.

Raman spectrum in cm^{-1}: 297(1b), 390(1b), 450(0b), 498(0b), 610(2), 624(4), 674(6), 686(4), 778(0), 835(6), 870(0), 931(4), 965-975(2b, db), 1044(1b), 1130(4b), 1186-1202(2b, db), 1355(1b), 1403(2b), 1422(2b), 1467(3b), 1700(6), 2880(2b), 2896(1b), 2928(6), 2954(3b), 2970(3b), 3010-3025(2b, db).

Dimethyl(2-methyl-2-cyclopropyl)cyclopropylcarbinol



A. To CH_3MgCl obtained from 10 g of Mg in 200 ml of absolute ether was added 21 g of the ethyl ester of 2-methyl-2-cyclopropylcyclopropanecarboxylic acid. The mixture was heated for 8-10 hr on a water bath and was then decomposed with water alone. The organic layer was dried with K_2CO_3 and distilled under vacuum in a fractionating column. A mixture of alcohols boiling at 86° at 25 mm was obtained, D^{20}_4 0.8850, $n^{20}D$ 1.4657, MR_D: found 48.24, calculated 47.11.

Found %: C 78.06, 77.96; H 11.50, 11.70. $C_{10}H_{18}O$. Calculated %: C 77.86; H 11.76.

Raman spectrum in cm^{-1}: 635(2b), 650(3), 710(5b), 717(5b), 763(1), 790(1), 813(1), 845(5b), 903(5b), 933(1), 970(2b), 1002(1), 1013(3b), 1041(2), 1102(1), 1172(3b), 1198(5), 1230(5), 1300(2), 1325(1), 1380(4b), 1398(2b), 1443 (3b), 1463(4b), 1600(3b), 1652(10), 287(3b), 2915(1b), 2935(2b), 2973(1b), 2997(3b), 3014(5b), 3080(10).

It is seen from the above spectroscopic data that isomerization of the three-membered ring took place, and a mixture of unsaturated alcohols was formed.

B. CH_3Li prepared from 4.5 g of metallic lithium and CH_3Cl in 200 ml of absolute ether was heated to 35°, and 17 g of the ethyl ester of 2-methyl-2-cyclopropylcyclopropanecarboxylic acid was added. The mixture was heated on a water bath for 8 hr, decomposed with water, and the aqueous layer extracted with ether. The ether solution was dried with $CaCl_2$ and distilled. This gave 11 g of an alcohol with a b. p. of 88.5-89° at 22 mm. The yield was 70%, D^{20}_4 0.9037, $n^{20}D$ 1.4595 MR_D: found 46.70, calculated 47.11.

Found %: C 77.36, 77.39; H 11.57, 11.80. $C_{10}H_{18}O$. Calculated %: C 77.86; H 11.76.

Raman spectrum in cm^{-1}: 258(0), 293(1b), 390(0), 408(0), 465(0), 630(0), 652(1), 668(1b), 712(2b), 783(1b) 822(1b), 832(1b), 845(2), 863(1), 880(0), 903(1b), 934(1), 948(1), 968(1), 1069(0), 1093(0), 1130(0), 1177(1b), 1195(5), 1250(0), 1298(1b), 1400(1b), 1422(1), 1452(2b), 1460(2b), 2865(2b) 2910(3b), 2932(3b), 2968(3b), 3000(10), 3065(3b).

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A NEW METHOD FOR THE SYNTHESIS OF CHLORIDES AND BROMIDES OF AROMATIC ACIDS

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(Presented by Academician M. I. Kabachnik, January 2, 1961)
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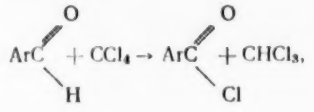
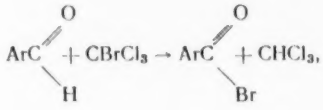
The reaction between an aldehyde and a chlorinating agent forms the basis of one of the relatively large number of methods for the synthesis of acid chlorides. Thus, benzoyl chloride is obtained by the reaction of benzaldehyde with chlorine [1], sulfur monochloride [2], sulfuryl chloride [3], or ethyl hypochlorite [4]. Among the syntheses having significance as preparative methods, we may point out, as an example, the preparation of o-chlorobenzoyl chloride from o-chlorobenzaldehyde and chlorine [5].

In a brief communication [6], Winstein and Seubold described the reaction of isovaleraldehyde or β-phenylisovaleraldehyde with carbon tetrachloride, which takes place in the presence of benzoyl peroxide. The reaction gave 60 and 55% yields of the chlorides of the corresponding acids. The present paper reports the results of a continuation of our investigation of the thermal reactions of CCl_4 [7, 8]. We have found that CCl_4 reacts with aromatic aldehydes at 180-205° and in the absence of benzoyl peroxide to form the acid chlorides in high yields (see the table):



where Ar is C_6H_5, p-$CH_3C_6H_4$, p-$CH_3OC_6H_4$, m-ClC_6H_4, p-ClC_6H_4, or α-$C_{10}H_7$. Like the carbon tetrachloride reactions, the reaction of bromotrichloromethane with aldehydes proceeds smoothly and also results in high yields of the acid bromides:



where Ar is C_6H_5 or p-$CH_3OC_6H_4$.

With both of the above halides, the amount of chloroform formed usually corresponded to the amount of acid halide obtained. No reaction was observed between aromatic aldehydes and chloroform.

During the reaction of CCl_4 with p-methylbenzaldehyde, exchange of chlorine for a hydrogen of the side chain occurred in addition to the main reaction. The formation of hydrogen chloride and tar in these experiments was usually insignificant. On the contrary, tar formation was very high during the reaction of cinnamaldehyde or furaldehyde with CCl_4; no acids chlorides were present amont the reaction products. The formation of acid chlorides and chloroform was likewise not observed in the reaction with m- and p-nitrobenzaldehydes; the formation of phosgene, hydrogen chloride, and tar did occur.

The yield of benzoyl chloride was considerably lower when the reaction of CCl_4 with benzaldehyde was carried out in an atmosphere of nitrogen. This leads to the conclusion that traces of peroxides, which are usually formed during the interaction of aldehydes and oxygen, initiated the reaction. The introduction of inhibitors (hydroquinone, pyrocatechol) led to an insignificant decrease in the yield of benzoyl chloride and chloroform. The increase in the amount of chloroform relative to the amount of acid chloride in this case indicates a reaction between the CCl_4 and the inhibitor. The introduction of inhibitor promoted tar formation.

Aldehyde	Temp., °C	Heating time, hours	Yield of $CHCl_3$, %	Acid halide (yield in %)	B. p. of acid halide, °C (mm Hg)	n_D	M. p. of anilide, °C
Reaction of CCl_4 with aldehydes*							
Benzaldehyde	200—205	12	91,9	Benzoyl chloride (93.9)	43 (2)	n_D^{20}1,5535	162
p-Methylbenzaldehyde	200—205	16	75,5	p-Methylbenzoyl chloride (58.0)	105—115 (10)	n_D^{20} —	147—148
p-Methoxybenzaldehyde	205—210	12	92,3	p-Methoxybenzoyl chloride (84.8)	105—107 (2)	n_D^{20}1,5811	171
m-Chlorobenzaldehyde	200—205	18	78,2	m-Chlorobenzoyl chloride (77.9)	101—102 (12)	$n_D^{20.5}$1,5682	122—125
p-Chlorobenzaldehyde	200—205	16	60,3	p-Chlorobenzoyl chloride (71.3)	103—104 (12)	n_D^{20}1,5783	194
α-Naphthaldehyde	180—185	11	71,1	α-Naphthoyl chloride (67.7)	128—131 (3)	n_D^{21}1,6473	161
Reaction of $CBrCl_3$ with aldehydes*							
Benzaldehyde	200—205	17	88,8	Benzoyl bromide (87.9)	55—59 (2)	n_D^{22}1,5841	162
p-Methoxybenzaldehyde	175—180	8	92,1	p-Methoxybenzoyl bromide (86.3)	147—153 (14)	n_D^{20}1,6177	171

*Mole ratio of halide to aldehyde of 5:1.

The addition of cuprous chloride in certain cases caused a very small increase in the yield of acid chloride.

EXPERIMENTAL

The experiments were carried out in heavy-wall glass tubes. The tubes were charged with the carefully purified reaction mixture, sealed, and heated in a Carius furnace. The reaction mixture was distilled in an efficient fractionating column. The amount of chloroform was determined in a manner similar to that described in [8]. After distillation of the unreacted carbon tetrachloride (or bromotrichloromethane), the residue (the acid halide) was distilled under vacuum. The acid halide was identified by boiling point and index of refraction; in addition, the corresponding anilide was prepared.

Our work along this line continues.

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THE SEQUENCE OF REACTIONS DURING HYDROGENATION OF 2,3-DIMETHYL-1,3-BUTADIENE OVER SKELETAL NICKEL CATALYST

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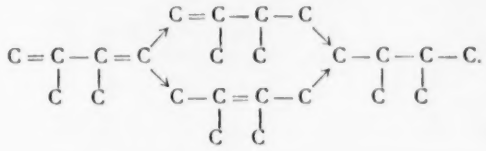
Original article submitted February 19, 1961

The hydrogenation of 2,3-dimethyl-1,3-butadiene has repeatedly been used as a model reaction in studies of the mechanism of the addition of hydrogen to conjugated diene systems. Two monoolefins (2,3-dimethyl-1-butene and 2,3-dimethyl-2-butene) and one paraffin can be formed by hydrogenation of 2,3-dimethyl-1,3-butadiene.



According to the data of Lebedev [1], the reaction is not selective in the presence of Pt black; after the addition of one mole of hydrogen, the hydrogenation product contains 2,3-dimethylbutane (28%) in addition to the monoolefins. Dupont [3] found that the process proceeds selectively over skeletal nickel catalyst; after the absorption of one mole of hydrogen, only monoolefins – 63% 2,3-dimethyl-1-butene and 37% 2,3-dimethyl-2-butene – are found in the catalyzate. Gostunskaya, Loza and Kazanskii [2] investigated the hydrogenation of this diene over Pt, Pd, and Ni catalysts. In the presence of skeletal nickel, 66.6% 2,3-dimethyl-1-butene, 25.5% 2,3-dimethyl-2-butene, and 8.3% of the original diene were separated from the reaction products obtained after the addition of one mole of hydrogen.

Thus, the course of the addition of hydrogen was established in the investigations cited above. However, the degree of selectivity was determined from the composition of the catalyzate at only one point – when one mole of hydrogen had been absorbed. The lack of a convenient and accurate method of analyzing the hydrocarbon mixtures formed during the reaction has hampered investigation of the kinetics of the individual stages.

The hydrogenation of 2,3-dimethylbutadiene in the presence of skeletal nickel catalyst was studied in the present work. The use of gas-liquid partition chromatography permitted us to carry out a complete analysis of the catalyzate during the course of the reaction and thereby to study the kinetics of the process and the sequence of the individual stages. The hydrogenation was carried out in a bomb at 25° with vigorous agitation (800 oscillations of the rocker per minute). The original diene had a b. p. of 69-70° and n_D^{20} 1.4310. Chromatographic analysis showed other hydrocarbons to be absent. The catalyst was prepared by leaching an Ni–Al alloy (1:1) with a 25% aqueous solution of sodium hydroxide. In each experiment, 0.2 g of catalyst and 0.01 mole of diene in 20 ml of solvent (methanol or 96% ethyl alcohol) were used. Samples for analysis were taken from the bomb during the course of the reaction. β,β'-Hydroxydipropionitrile was used as the stationary phase in the chromatographic analyses. The fractions taken from the chromatographic column were burned and converted to hydrogen by the method of [4]. The detector was first calibrated for the individual hydrocarbons.

Kinetic curves of the hydrogenation of 2,3-dimethylbutadiene in methyl and ethyl alcohols are presented in Fig. 1. It is apparent from Fig. 1 that in either solvent the first mole of hydrogen is absorbed at a constant rate – 20 ml/minute in methyl alcohol and 15.3 ml/minute in ethyl alcohol. Further hydrogenation proceeds at a constantly decreasing rate, and hydrogenation practically stops after absorption of 1.6 moles of hydrogen. In the hydrogen-consumption calculations, a correction for the fugacity of the hydrocarbon was introduced; the correction was determined by analyzing the composition of the gas phase.

The change in catalyzate composition with an increase in the amount of hydrogen absorbed is shown in the table and in Fig. 2. These data show that this relationship is just the same in the two solvents. Both olefins are formed simultaneously during the absorption of the first mole of hydrogen. The concentration of these olefins in the catalyzate increases linearly with the increase in the amount of hydrogen absorbed. Figure 1 shows the relationship between the rate of formation of each monoolefin and the amount of hydrogen absorbed, as calculated from chromatographic analyses of the catalyzates. As may be seen from Fig. 1, the rates of formation of 2,3-dimethyl-1-butene (curve III) and of 2,3-dimethyl-2-butene (curve IV) in both alcohols are constant, and although the rates differ, the ratio of the rates also remains constant (3 : 2).

Composition of Reaction Products from the Hydrogenation of 2,3-Dimethyl-1,3-butadiene in Methyl Alcohol

Catalyzate composition, mole %	H_2 absorbed, molar equivalents									
	0,17	0,28	0,48	0,69	0,93	1,03	1,11	1,21	1,39	1,69
2,3-Dimethyl-1,3-butadiene	82,5	72,3	50,5	29,7	4,9	—	—	—	—	—
2,3-Dimethyl-1-butene	9,8	16,2	31,4	43,0	58,2	60,4	51,1	42,0	21,4	—
2,3-Dimethyl-2-butene	7,7	11,5	18,1	27,3	36,9	38,2	38,5	38,7	39,8	41,6
2,3-Dimethylbutane	—	—	—	—	—	1,4	10,4	19,8	38,4	58,4

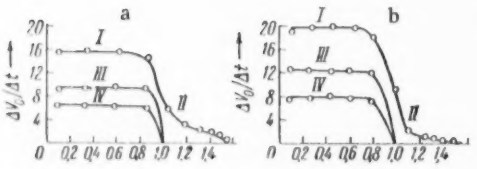


Fig. 1. Hydrogenation of 2,3-dimethyl-1,3-butadiene in ethyl alcohol (a) and in methyl alcohol (b); I) overall rate of formation of monoolefins; II) rate of formation of 2,3-dimethylbutane; III) 2,3-dimethyl-1-butene; IV) 2,3-dimethyl-2-butene (the moles of hydrogen absorbed are plotted along the abscissa).

Hydrogenation of the diene was strictly selective under the conditions used. When one mole of hydrogen had been absorbed, the mixture consisted of 62% 2,3-dimethyl-1-butene and 38% 2,3-dimethyl-2-butene, and neither diene nor paraffin was present in the catalyzate. During the absorption of the second mole of hydrogen, the concentration of 2,3-dimethyl-1-butene in the catalyzate decreased linearly, and there was a corresponding increase in the concentration of 2,3-dimethylbutane. At the same time, the 2,3-dimethyl-2-butene content of the catalyzate not only did not decrease, it even increased somewhat (by 3-4%). At the time that 1.6 moles of hydrogen had been absorbed, the 2,3-dimethyl-1-butene had completely disappeared from the solution, and the reaction had practically ceased. The residual 2,3-dimethyl-2-butene hydrogenated extremely slowly; hydrogen was absorbed at a rate of 1 ml/hr.

The insignificant increase in the concentration of 2,3-dimethyl-2-butene in the catalyzate during the addition of the second mole of hydrogen could be explained by the slow isomerization of 2,3-dimethyl-1-butene. For confirmation of this assumption, hydrogenation of 2,3-dimethyl-1-butene (b. p. 55.2-56.6°; $n^{20}D$ 1.3902), prepared by hydrogenation of 2,3-dimethyl-1,3-butadiene over skeletal nickel and separated by fractionation in a column, was studied under analogous conditions. A trace (1%) of 2,3-dimethylbutane in this olefin was detected chromatographically. Figure 3 presents the relationship between catalyzate composition and depth of hydrogenation. It is apparent from Fig. 3 that some isomerization of the 2,3-dimethyl-1-butene to 2,3-dimethyl-2-butene did take place during the course of hydrogenation. Up to 4% of the latter olefin had accumulated in the solution by the end of the reaction. When 2,3-dimethyl-1-butene was agitated in a nitrogen atmosphere with skeletal nickel catalyst saturated with hydrogen, no isomerization was observed, but part of the olefin (3%) was hydrogenated by the hydrogen adsorbed on the catalyst.

The results of our work show that 2,3-dimethylbutadiene hydrogenates strictly selectively over skeletal nickel catalyst in an alcohol medium; the monoolefins formed are not hydrogenated during the absorption of the first mole of hydrogen. Moreover, the 2,3-dimethyl-1-butene and 2,3-dimethyl-2-butene are formed at a constant rate in a ratio of 3 : 2.

In the second stage, the 2,3-dimethyl-1-butene is first hydrogenated selectively, and a slight amount of isomerization of the α-olefin to the β-olefin is observed during the course of the hydrogenation. 2,3-Dimethyl-2-butene is apparently weakly adsorbed and hydrogenates very slowly. The observed sequence of reactions is thus dictated by adsorptive displacement of monoolefins by the diene, the first stage, and of the β-olefin by α-olefin, in the second.

Since 2,3-dimethyl-1-butene isomerizes extremely slowly and is displaced by the diene, the formation of 2,3-dimethyl-2-butene may be considered to be the result of the addition of hydrogen to the diene in the 1 and 4 positions, if the possibility of isomerization of the α-olefin at the instant of its formation and before its desorption is ignored.

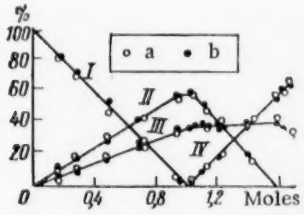


Fig. 2. Dependence of catalyzate composition on amount of hydrogen absorbed. I) 2,3-Dimethyl-1,3-butadiene; II) 2,3-dimethyl-1-butene; III) 2,3-dimethyl-2-butene; IV) 2,3-dimethylbutane. a) in methyl alcohol; b) in ethyl alcohol (the moles of hydrogen absorbed are plotted along the abscissa).

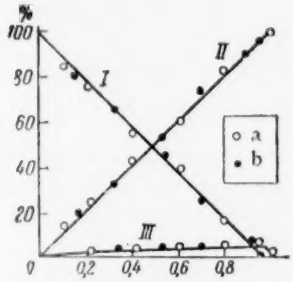


Fig. 3. Dependence of catalyzate composition on amount of hydrogen absorbed. I) 2,3-Dimethyl-1-butene; II) 2,3-dimethylbutane; III) 2,3-dimethyl-2-butene. a) In methyl alcohol; b) in ethyl alcohol (the moles of hydrogen absorbed are plotted along the abscissa.

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THE THERMAL CONDUCTIVITY AND VISCOSITY OF ZIRCONIUM AND HAFNIUM TETRACHLORIDE VAPORS OVER THE TEMPERATURE INTERVAL 300-700°

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The development of new methods of separation of zirconium and hafnium tetrachlorides requires a knowledge of the constants characterizing molecular transfer processes, such as viscosity of the vapor, vapor-phase thermal conductivity, heat content, etc. We have determined the thermal conductivities and viscosities of zirconium and hafnium tetrachloride vapors over the temperature interval of 300-700°

1. Determination of the thermal conductivities of $ZrCl_4$ and $HfCl_4$ vapors. The vapor thermal conductivities were determined by the "hot wire" method. The method involves heating a fine wire in an atmosphere of the given gas by means of an electric current; the resistance of the wire at constant power input depends on its temperature and, consequently, on the thermal conductivity of the gas.

The measurements were carried out with a special apparatus (Fig. 1), which included of a double furnace with Dural blocks. The temperature of the blocks was measured with an EPP-09 automatic electronic potentiometer and a platinum–rhodium thermocouple; the temperature was controlled to within ±1°C. The glass thermal conductivity cell was placed in the furnace. The cell consisted of a Pyrex glass tube with a diameter of 5-7 mm, along the axis of which was stretched a platinum wire with a diameter of 0.05 mm. In the top of the tube was sealed a platinum lead, to which the central wire was welded. The temperature of the tube wall was measured with a platinum resistance thermometer, which was double wound on the tube. The lower part of the tube was sealed to a larger tube with a diameter of 12-15 mm. A load and an electrically conducting spring were contained in the larger tube. A platinum lead was sealed in the bottom of this tube, and a side arm for introduction of the gas under investigation was sealed to the side of the tube. The temperature of the platinum wire was determined by its resistance, which was measured with a bridge circuit. One of the arms of the bridge was the platinum wire. Moreover, the resistance of the fine wire was also calculated by Ohm's law.

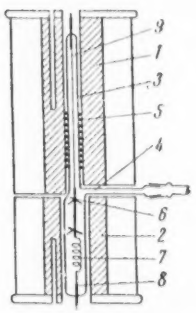

Fig. 1. Schematic diagram of apparatus used for the determination of the thermal conductivities of zirconium and hafnium tetrachloride vapors. 1,2) Dural blocks; 3) cell; 4) side arm with ground glass joint; 5) resistance thermometer; 6) load with centering devices; 7) platinum wire spring; 8) electrical lead.

During the course of an experiment, the resistance of the platinum wire and of the resistance thermometer were measured at room temperature, and graphs were constructed of the dependence of each of these resistances on temperature. The cell was then placed in the furnace, and measurements of the dependece of heat transfer between the platinum wire and the walls of the tube on the power input to the heated wire were carried out at different wall temperatures; the measurements were carried out under vacuum (10^{-3} mm Hg) and in an atmosphere of dry hydrogen. The cell was then charged with zirconium or hafnium tetrachloride powder, pumped to a pressure of 10^{-3} mm Hg, sealed, and again placed in the furnace. The temperature of the lower block was brought to 300-320°. The pressure of the tetrachloride vapor at this temperature was approximately 0.75 atm; however, the thermal conductivity of the vapor does not depend on pressure. The temperature of the upper block was varied from 350 to 500°. The measurements were carried out as follows: At a given cell-wall temperature, the temperature of the central wire was measured while the power input was varied. The

determinations were carried out at cell-wall temperatures ranging from 350 to 500°. The results of the measurements were used to construct graphs showing the variation in W with ΔT at given wall temperatures and the variation in W with wall temperature at constant $\Delta T = 20°$. The thermal conductivity of the tetrachloride vapor was calculated by means of the equation [1, 2]

$$\lambda = \frac{\lambda_1 (W_2 - W_0)}{W_1 - W_0},$$

where λ_1 is the thermal conductivity of hydrogen at the given temperature and W_0, W_1, W_2 are the powers required to produce a temperature differential of 20° under vacuum, in hydrogen, and in tetrachloride vapor, respectively.

TABLE 1. Dependence of the Coefficient of Thermal Conductivity on $ZrCl_4$ and $HfCl_4$ Vapors on Temperature

Temp., °C	$\lambda \cdot 10^5$ cal/cm/sec/degree	
	$ZrCl_4$	$HfCl_4$
300	4,31	3,67
350	4,87	3,95
400	5,43	4,26
450	5,96	4,58
500	6,35	4,89

TABLE 2. Dependence of the Coefficient of Viscosity of $ZrCl_4$ and $HfCl_4$ Vapors on Temperature

Temp., °C	$\eta \cdot 10^7$ poises	
	$ZrCl_4$	$HfCl_4$
300	1970	2680
400	2265	3060
500	2640	3505
600	2970	3870
700	3230	4150

The results are presented in Table 1 and Fig. 2. As would be expected, the thermal conductivity coefficients of zirconium and hafnium tetrachloride vapors increase with an increase in temperature. The relationship is linear. The thermal conductivity of $ZrCl_4$ vapor is higher than that of $HfCl_4$ vapor, and the difference increases with an increase in the temperature from 300 to 500°. Thus, at 300° the coefficients of thermal conductivity of $ZrCl_4$ and $HfCl_4$ were, respectively, $4.31 \cdot 10^5$ and $3.67 \cdot 10^5$, while at 500° they were $6.35 \cdot 10^5$ and $4.89 \cdot 10^5$ cal/cm·sec·degree, respectively.

2. Determination of the viscosities of $ZrCl_4$ and $HfCl_4$ vapors. The viscosities of the tetrachloride vapors were determined by flowing the vapor through a capillary [3, 4]. The coefficient of viscosity was calculated by the Hagen-Poiseuille equation using the following experimentally determined values: the vapor pressure at the inlet and outlet of the capillary, the mass flowing through the capillary in a known time, the dimensions of the capillary.

The apparatus used for the measurements is shown schematically in Fig. 3. It comprised a two-section furnace with nickel and Dural blocks. The temperature of the nickel block was measured and controlled over the temperature range 350-700° with an accuracy of ± 1.5° by means of an EPV-2 automatic electronic potentiometer. The temperature of the Dural block was measured with a chromel-alumel thermocouple and a PP potentiometer, and it was controlled by means of a separate temperature control system with an accuracy of ± 0.3° over the temperature range 250-350°. A quartz ampoule with the capillary sealed to it was placed in the furnace. The ampoule was charged with freshly sublimed zirconium or hafnium tetrachloride. It was equipped with a thermocouple well. The radius of the capillary was determined with an accuracy of ± 0.003 mm by measuring the length of a mercury column in the capillary with a comparator and weighing the mercury on an analytical balance.

The measurements were carried out as follows. The ampoule was filled to approximately 1/3 its volume with freshly sublimed zirconium or hafnium tetrachloride powder, and the tube was sealed and the ampoule weighed. The thermocouple was inserted into the well, and the entire ampoule was placed in the furnace blocks, which had been heated to the desired temperatures. The ampoule was located so that the capillary was in the nickel block and the bulb in the Dural block. The ampoule was held in the furnace for 5-10 minutes, after which it was removed, cooled, and weighed to determine the amount of tetrachloride which had passed through the capillary. The vapor pressure inside the ampoule was calculated from the temperature by means of the equations [5]:

$$\lg P_{мм} = -\frac{5400}{T} + 11{,}766 \text{ for } ZrCl_4 \quad \text{and} \quad \lg P_{мм} = -\frac{5197}{T} + 11{,}712 \text{ for } HfCl_4.$$

The temperature of the Dural block was chosen so that the pressure inside the ampoule would be 200 mm Hg. The coefficient of viscosity of the vapor at a given temperature was calculated by means of the following equation, which includes a correction for expansion of the gas in the capillary:

$$\eta = \frac{\pi \cdot r^4 \cdot \tau \cdot \rho}{8ML} \cdot \frac{p_1^2 - p_2^2}{2p_1},$$

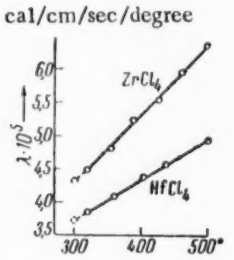

Fig. 2. Dependence of the thermal conductivity of zirconium and hafnium tetrachloride vapors on temperature.

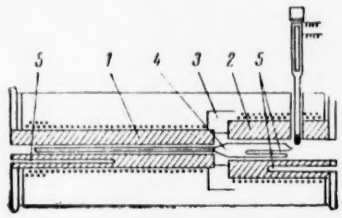

Fig. 3. Schematic diagram of the apparatus used for the determination of the viscosity of zirconium and hafnium tetrachloride vapors. 1) Nickel block; 2) Dural block; 3) ceramic ring; 4) ampoule and capillary; 5) thermocouple wells.

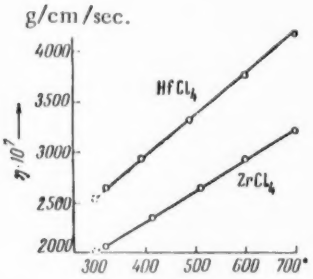

Fig. 4. Dependence of the viscosities of zirconium and hafnium tetrachloride vapors on temperature.

where, r is the radius of the capillary, p_1 is the pressure inside the ampoule, p_2 is atmospheric pressure, τ is the time, M is the loss in weight of the ampoule, L is the length of the capillary, and ρ is the density of the vapor in the capillary at the pressure and temperature of the capillary, which was calculated by means of the gas law assuming the vapor to be an ideal gas; this assumption is completely justifiable at the given temperature and pressure. The measurements were carried out over the temperature interval 350-700°. The results are presented in Table 2 and Fig. 4.

The coefficients of viscosity were directly proportional to temperature over the temperature interval investigated, and the viscosity of $HfCl_4$ vapor somewhat exceeded the viscosity of $ZrCl_4$ vapor. Thus, for example, at 500°, $\eta_{ZrCl_4} = 2640 \cdot 10^{-7}$ poise and η_{HfCl_4} was $3505 \cdot 10^{-7}$ poise. It should be noted that the viscosity of $HfCl_4$ vapor increased to a somewhat greater extent with an increase in temperature than did $ZrCl_4$ vapor.

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Soviet Journals Available in Cover-to-Cover Translation

ABBREVIATION	RUSSIAN TITLE	TITLE OF TRANSLATION	PUBLISHER	TRANSLATION BEGAN Vol.	Issue	Year
AÉ	Atomnaya énergiya	Soviet Journal of Atomic Energy	Consultants Bureau	1	1	1956
Akust. zh.	Akusticheskii zhurnal	Soviet Physics – Acoustics	American Institute of Physics	1	1	1955
	Antibiotiki	Antibiotics	Consultants Bureau	4	1	1959
Astr(on). zh(urn).	Astronomicheskii zhurnal	Soviet Astronomy–AJ	American Institute of Physics	34	1	1957
Avto(mat). svarka	Avtomaticheskaya svarka	Automatic Welding	British Welding Research Association (London)		1	1959
	Avtomatika i Telemekhanika	Automation and Remote Control	Instrument Society of America	27	1	1956
	Biofizika	Biophysics	National Institutes of Health*		1	1957
	Biokhimiya	Biochemistry	Consultants Bureau	21	1	1956
Byull. éksp(erim). biol. i med.	Byulleten' éksperimental'noi biologii i meditsiny	Bulletin of Experimental Biology and Medicine	Consultants Bureau	41	1	1959
DAN (SSSR) / Dokl(ady) AN SSSR	Doklady Akademii Nauk SSSR	The translation of this journal is published in sections, as follows:				
		Life Sciences: Doklady Biochemistry Section	American Institute of Biological Sciences	106	1	1956
		Life Sciences: Doklady Biological Sciences Sections (Includes: Anatomy, biophysics, cytology, ecology, embryology, endocrinology, evolutionary morphology, genetics, histology, hydrobiology microbiology, morphology, parasitology, physiology, zoology sections)	American Institute of Biological Sciences	112	1	1957
		Life Sciences: Doklady Botanical Sciences Sections (Includes: Botany, phytopathology, plant anatomy, plant ecology, plant embryology, plant physiology, plant morphology sections)	American Institute of Biological Sciences	112	1	1957
		Chemical Sciences: Proceedings of the Academy of Sciences of the USSR, Section: Chemical Technology	Consultants Bureau	106	1	1956
		Chemical Sciences: Proceedings of the Academy of Sciences of the USSR, Section: Chemistry	Consultants Bureau	106	1	1956
		Chemical Sciences: Proceedings of the Academy of Sciences of the USSR, Section: Physical Chemistry	Consultants Bureau	112	1	1957
		Earth Sciences: Doklady Earth Sciences Sections (Includes: Geochemistry, geology, geophysics, hydrogeology, mineralogy, paleontology, petrography, permafrost sections)	American Geological Institute	124	1	1959
		Earth Sciences: Proceedings of the Academy of Sciences of the USSR, Section: Geochemistry	Consultants Bureau	106-123	1-6	1957-1958
		Earth Sciences: Proceedings of the Academy of Sciences of the USSR, Sections: Geology	Consultants Bureau	106-123	1-6	1957-1958
		Mathematics: Doklady Soviet Mathematics	The American Mathematics Society	131	1	1961
		Physics: Soviet Physics–Doklady (Includes: Aerodynamics, astronomy, crystallography, cybernetics and control theory, electrical engineering, energetics, fluid mechanics, heat engineering, hydraulics, mathematical physics, mechanics, physics, technical physics, theory of elasticity sections)	American Institute of Physics	106	1	1956
		Physics: Proceedings of the Academy of Sciences of the USSR, Applied Physics Sections (does not include mathematical physics or physics sections)	Consultants Bureau	106-117	1	1956-1957
Derevoobrabat. prom-st'.	Derevoobrabatyvayushchaya promyshlennost'	Wood Processing Industry	Timber Development Association (London)		9	1959
	Élecktrosvyaz	Telecommunications	Massachusetts Institute of Technology*		1	1957
Éntom(ol). oboz(renie)	Éntomologicheskoe obozrenie	Entomological Review	American Institute of Biological Sciences	38	1	1959
Farmakol. (i) toksikol(ogiya)	Farmakologiya i toksikologiya	Pharmacology and Toxicology	Consultants Bureau	20	1	1957
FMM	Fizika metallov i metallovedenie	Physics of Metals and Metallography	Acta Metallurgica*	5	1	1957
Fiziol. zhurn. SSSR (im. Sechenova)	Fiziologicheskii zhurnal im. I. M. Sechenova	Sechenov Physiological Journal USSR	National Institutes of Health*		1	1957
Fiziol(ogiya) rast.	Fiziologiya rastenii	Plant Physiology	American Institute of Biological Sciences	4	1	1957
	Geokhimiya	Geochemistry	The Geochemical Society		1	1958
FTT	Fizika tverdogo tela	Soviet Physics–Solid State	American Institute of Physics	1	1	1959
Izmerit. tekh(nika)	Izmeritel'naya tekhnika	Measurement Techniques	Instrument Society of America		1	1959
Izv. AN SSSR, O(td). Kh(im). N(auk)	Izvestiya Akademii Nauk SSSR: Otdelenie khimicheskikh nauk	Bulletin of the Academy of Sciences of the USSR: Division of Chemical Sciences	Consultants Bureau		1	1952

continued

Izv. AN SSSR, O(td). T(ekhn). N(auk): Met(all). i top.	(see Met. i top.)				
Izv. AN SSSR Ser. fiz(ich).	Izvestiya Akademii Nauk SSSR: Seriya fizicheskaya	Bulletin of the Academy of Sciences of the USSR: Physical Series	Columbia Technical Translations	1	1954
Izv. AN SSSR Ser. geofiz.	Izvestiya Akademii Nauk SSSR: Seriya geofizicheskaya	Bulletin (Izvestiya) of the Academy of Sciences USSR: Geophysics Series	American Geophysical Union	1	1954
Izv. AN SSSR Ser. geol.	Izvestiya Akademii Nauk SSSR: Seriya geologicheskaya	Izvestiya of the Academy of Sciences of the USSR: Geologic Series	American Geological Institute	1	1958
Kauch. i rez.	Kauchuk i rezina	Soviet Rubber Technology	Research Association of British Rubber Manufacturers	18	1 1959
	Kinetika i kataliz	Kinetics and Catalysis	Consultants Bureau	1	3 1960
	Koks i khimiya	Coke and Chemistry USSR	Coal Tar Research Association (Leeds, England)		1 1958
Kolloidn. zh(urn).	Kolloidnyi zhurnal	Colloid Journal	Consultants Bureau	14	1 1952
	Kristallografiya	Soviet Physics – Crystallography	American Institute of Physics	2	1 1957
Metalov. i term. obrabot. metal.	Metallovedenie i termicheskaya obrabotka metallov	Metal Science and Heat Treatment of Metals	Acta Metallurgica	6	1 1958
	Metallurg	Metallurgist	Acta Metallurgica		1 1957
Met. i top.	Metallurgiya i topliva	Russian Metallurgy and Fuels	Eagle Technical Publications		1 1960
Mikrobiol.	Mikrobiologiya	Microbiology	American Institute of Biological Sciences	26	1 1957
OS	Optika i spektroskopiya	Optics and Spectroscopy	American Institute of Physics		6 1959
	Pochvovedenie	Soviet Soil Science	American Institute of Biological Sciences		1 1958
	Priborostroenie	Instrument Construction	British Scientific Instrument Research Association		1 1959
Pribory i tekhn. éks(perimenta)	Pribory i tekhnika éksperimenta	Instruments and Experimental Techniques	Instrument Society of America		1 1957
Prikl. matem. i mekh.	Prikladnaya matematika i mekhanika	Applied Mathematics and Mechanics	American Society of Mechanical Engineers		1 1958
PTÉ	(see Pribory i tekhn. éks.)				
	Problemy Severa	Problems of the North	National Research Council of Canada		
Radiotekh.	Radiotekhnika	Radio Engineering	Massachusetts Institute of Technology*	12	1 1957
Radiotekh. i élektronika	Radiotekhnika i élektronika	Radio Engineering and Electronics	Massachusetts Institute of Technology*	2	1 1957
	Stanki i instrument	Machines and Tooling	Production Engineering Research Assoc.		1 1959
	Stal'	Stal (In English)	Iron and Steel Institute		1 1959
Stek. i keram.	Steklo i keramika	Glass and Ceramics	Consultants Bureau	13	1 1956
Svaroch. proiz-vo	Svarochnoe proizvodstvo	Welding Production	British Welding Research Association		4 1959
Teor. veroyat. i prim.	Teoriya veroyatnostei i ee primenenie	Theory of Probability and Its Applications	Society for Industrial and Applied Mathematics		1 1956
Tsvet. Metally	Tsvetnye metally	Nonferrous Metals	Primary Sources		1 1960
UFN	Uspekhi fizicheskikh Nauk	Soviet Physics – Uspekhi (partial translation)	American Institute of Physics	66	1 1958
UKh	Uspekhi khimii	Russian Chemical Reviews	The Chemical Society (London)		1 1960
UMN	Uspekhi matematicheskikh nauk	Russian Mathematical Surveys	London Mathematical Society	15	1 1960
Usp. fiz. nauk	(see UFN)				
Usp. khim(ii)	(see UKh)				
Usp. matem. nauk	(see UMN)				
Usp. sovr. biol.	Uspekhi sovremennoi biologii	Russian Review of Biology	Oliver and Boyd	48	1959
Vest. mashinostroeniya	Vestnik mashinostroeniya	Russian Engineering Journal	Production Engineering Research Assoc.	4	1959
Vop. gem. i per. krovi	Voprosy gematologii i perelivaniya krovi	Problems of Hematology and Blood Transfusion	National Institutes of Health*	1	1957
Vop. onk.	Voprosy onkologii	Problems of Oncology	National Institutes of Health*	1	1957
Vop. virusol.	Voprosy virusologii	Problems of Virology	National Institutes of Health*	1	1957
Zav(odsk). lab(oratoriya)	Zavodskaya laboratoriya	Industrial Laboratory	Instrument Society of America	25	1 1959
ZhAKh Zh. anal(it). khimii	Zhurnal analiticheskoi khimii	Journal of Analytical Chemistry USSR	Consultants Bureau	7	1 1952
ZhETF Zh. éksperim. i teor. fiz.	Zhurnal éksperimental'noi i teoreticheskoi fiziki	Soviet Physics–JETP	American Institute of Physics	28	1 1955
ZhFKh Zh. fiz. khimii	Zhurnal fizicheskoi khimii	Russian Journal of Physical Chemistry	The Chemical Society (London)		7 1959
ZhMÉI Zh(urn). mikrobiol. épidemiol. i immunobiol.	Zhurnal mikrobiologii, épidemiologii i immunobiologii	Journal of Microbiology, Epidemiology and Immunobiology	National Institutes of Health*		1 1957
ZhNKh Zh(urn). neorgan(ich). khim(ii)	Zhurnal neorganicheskoi khimii	The Russian Journal of Inorganic Chemistry	The Chemical Society (London)		1 1959
ZhOKh Zh(urn). obshch(ei) khimii	Zhurnal obshchei khimii	Journal of General Chemistry USSR	Consultants Bureau	19	1 1949
ZhPKh Zh(urn). prikl. khimii	Zhurnal prikladnoi khimii	Journal of Applied Chemistry USSR	Consultants Bureau	23	1 1950
ZhSKh Zh(urn). strukt. khimii	Zhurnal strukturnoi khimii	Journal of Structural Chemistry	Consultants Bureau	1	1 1960
ZhTF Zh(urn). tekhn. fiz.	Zhurnal teknicheskoi fiziki	Soviet Physics–Technical Physics	American Institute of Physics	26	1 1956
Zh(urn). vyssh. nervn. deyat. (im. Pavlova)	Zhurnal vysshei nervnoi deyatel'nosti (im. I. P. Pavlova)	Pavlov Journal of Higher Nervous Activity	National Institutes of Health*		1 1958

*Sponsoring organization. Translation through 1960 issues is a publication of Pergamon Press.

SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.- Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.-Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Metrology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

NOTE: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. –Publisher.

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